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Final Report for DOE NETL Gas Hydrate Project FWP 65213

Kinetic Parameters for the Exchange of Hydrate Formers

February 2019

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Abstract

This report documents the research activities sponsored by the U.S. Department of Energy, National Energy Technology Laboratory (NETL), by the Pacific Northwest National Laboratory (PNNL) for the gas hydrate project entitled, “Kinetic Parameters for the Exchange of Hydrate Formers.” This project started June 1, 2013 and concluded December 31, 2018, and comprised five budget periods, under FWP-65213. The overarching goal of this project was to gain an improved understanding of the dynamic processes of gas hydrate accumulations in geologic media by combining laboratory studies, numerical simulation, and analysis of shipboard infrared imaging of hydrate core samples. This project comprised four principal components: 1) fundamental laboratory investigations, 2) numerical simulator development and verification, 3) hydrate core characterization and analysis, and 4) applied laboratory and numerical investigations. Laboratory and field experiments have demonstrated the four core methodologies for producing natural gas hydrates from geologic formations: 1) depressurization, 2) thermal stimulation, 3) inhibitor injection, and 4) guest molecule exchange. Converting these methodologies into viable commercial technologies remains challenging, either from an economic or technical perspective. This project was largely focused with the technical challenges associated with the guest molecule exchange method, which is often referred to as gas swapping. Previous research by PNNL had shown that gas swapping with pure CO₂ was not feasible, as first originally thought, principally due to the formation of secondary hydrates, which clogged or reduced the effective permeability of the hydrate-bearing formation. This research was directed at discovering the potential for using mixtures of gases to affect the gas swapping methodology at commercial scales. The Ignik Sikumi Gas Hydrate Field Trial demonstrated the injection of a N₂-CO₂ gas mixture into a natural gas hydrate bearing layer, and exchange behavior with the CH₄ hydrate former or guest molecules. The original concept behind the use of a N₂-CO₂ was to maintain gas conditions at the reservoir state. Pure CO₂ would have existed under supercritical conditions, with an associated density closer to a liquid than gas. One of the key outcomes from this research project has been the discovery, through laboratory experiments and numerical simulation, that gas mixtures, especially those with components having different gas hydrate equilibria conditions provide a control option for the guest molecule exchange methodology. For example, the dissociation or formation of hydrate could be controlled by adjusting the composition of the gas mixture. This research project was dynamic in that the discoveries during each budget period would set the course of research during successive budget periods. Therefore, this report is arranged in chronological order progressing through the five budget periods of the project.

Executive Summary

Through the funding support of the U.S. Department of Energy, under this project FWP-65213, the Pacific Northwest National Laboratory (PNNL) investigated numerically and experimentally an unconventional technology for producing geologic accumulations of natural gas hydrates, often referred to as guest-molecule exchange or guest-molecule swapping. The project additionally investigated the geomechanical impacts of producing natural gas hydrates from geologic reservoirs, especially those which are suboceanic. The guest-molecule-exchange technology involves replacing methane molecules with the clathrate structure with alternative guest molecules, such as carbon dioxide and nitrogen. The alternative guest molecules are typically selected to maintain the original hydrate structure and be thermodynamically preferred under the reservoir temperature and pressure conditions. The numerical component of the work principally investigated the Ignik Sikumi Gas Hydrate Field Trial, a collaborative project conducted by the U.S. DOE National Energy Technology Laboratory, ConocoPhillips, and the Japan Oil, Gas, and Metals National Corporation on the Alaska North Slope. The numerical component of the work additionally investigated problems for which there are comparison data from laboratory experiments or comparable numerical simulator solutions. The experimental component of the research provided supporting kinetic exchange data, needed by the numerical simulations. Both the numerical and experimental elements are preliminary investigations due to the limited scope of the work. Funding for this work was supported over multiple budget periods. Five budget periods are delineated in this proposal. Budget Period 1 (BP1) spanned FY2013 and FY2014 and involved both experimental and numerical tasks. Budget Period 2 (BP2) spanned FY2014 and FY2015 and was limited to numerical simulation tasks. Budget Period 3 (BP3) spanned FY2015 and FY2016, was limited to numerical simulation tasks and was refocused from the guest-molecule exchange production technology to implementing geomechanics. Budget Period 4 (BP4) spanned FY2016 and FY2017, was limited to numerical simulation tasks, coupled with a KIGAM funded project, and considered both geomechanics and the guest-molecule exchange production technology. Budget Period 5 (BP5) spanned FY2017 and FY2018, with an emphasis on hydrate dissociation with nitrogen injection and verification of the developed geomechanics capabilities via an international code comparison study.

The title of this project was “Kinetic Parameters for the Exchange of Hydrate Formers,” which reflected the initial objective of the research. The STOMP-HYDT-KE had a kinetic formulation for modeling the formation and dissociation of gas hydrates, but also the exchange of the guest molecules. This formulation was developed in response to application of a predecessor version of the simulator that used an equilibrium formulation, against gas swapping experiments conducted at KIGAM. The equilibrium formulation was found to show poor agreement with the experiments due to the kinetics of the process. Switching from an equilibrium to kinetic formulation, meant tracking mass of hydrate formers in mobile and hydrate form independently, resulting in more equations per grid cell. When the new kinetic formulation was applied against the KIGAM gas swapping experiments, good agreement was found between the simulation results and the experimental observations. Whereas this result was a positive outcome, it left open the question of what parameters are appropriate for describing the kinetics associated with gas hydrate formation, dissociation and guest molecule exchange. This project determined those parameters from three separate experiments, two laboratory and one field. The first laboratory experiment was the original KIGAM exchange experiment, the second laboratory experiment was a similar exchange experiment conducted at PNNL, and field experiment was the Ignik Sikumi Gas Hydrate Field Trial. The parameters from these three experiments were found to be reasonably close, and now serve as the default parameters used in current STOMP-HYDT-KE simulations.

The start of BP3 saw a shift in research emphasis from guest molecule swapping to geomechanics, with the outcome of the depressurization demonstration in the Nankai Trough. Geomechanical modeling capabilities were not fully implemented in the STOMP simulator, and prior to starting the development of this capability some consideration was given to whether the capabilities should be implemented through existing commercial, academic, or national laboratory software, or to code from scratch. The Lawrence

Berkeley National Laboratory (LBNL) had previously approached the problem using commercial software, but recently switched to an internally developed geomechanics software package. PNNL decided to follow suit and code from scratch, mainly to keep the software as a research tool and the code developers familiar with the internal workings. To avoid the typical translations needed in modeling flow and transport using a finite-volume formulation and geomechanics using a finite-element formulation, the original hexahedral grid discretization was used in both implementations, yielding hexahedral elements. Limiting the capabilities to porothermoelastic reduced the initial development period, and the STOMP simulator now has geomechanical capabilities for modeling displacements in response to imposed stresses, pore pressure changes and temperature changes on a heterogeneous geomechanical property field, with hydrate saturation dependent properties.

PNNL had previously proposed a second international gas hydrate code comparison study with an emphasis on the guest molecule swapping production technology. This proposed study has yet to be supported by NETL, but prior to the start of BP5 there was growing interest in a second international gas hydrate code comparison study with an emphasis on coupled thermal, hydraulic, thermodynamic and geomechanical processes. After a preliminary meeting, held at LBNL, the study got underway with three co-leads: Mark White at PNNL, Tim Kneafsey at LBNL, and Yongkoo Seol at NETL. This study, referred to as IGHCCS2, involves many of the participants from the first international code comparison study, but also many more from the United States, Korea, Japan, Germany, United Kingdom, and China. The study uses teleconferences to develop problems, discuss numerical simulators and solution schemes, and compare solution submissions. There are currently five problems, which are considered to be benchmark in scale, each with a problem champion. Problem champions are responsible for developing problem descriptions, providing initial solutions, shepherding problem discussions, and assisting in the study publications. At the conclusion of the benchmark problem series, we anticipate the study transitioning into a challenge problem stage; where, problems will be field oriented and have both a simulator and practitioner aspect. All of the benchmark problems involve hydrate dissociation, and four require coupled geomechanics. When published, we anticipate these problems to define the state of numerical simulation for modeling gas hydrate systems, and to serve as benchmarks for future code developers. A more immediate benefit of the study is the verification of the coupled hydrate and geomechanical modeling capabilities in STOMP-HYDT-KE.

Acknowledgments

PNNL recognizes the financial support of the U.S. Department of Energy, National Energy Technology Laboratory (NETL) over the last decade for both its experimental and numerical research activities focused on understanding gas hydrate systems and the development of gas hydrate production technologies. In particular the NETL Gas Hydrate Program has supported the development and advancement of the suite of STOMP hydrate numerical simulators. Numerical simulation application and advancement is an iterative process, where numerical simulation applications against laboratory or field experiments often reveal deficiencies in modeling approaches, that spur new developments. At PNNL this iterative progression has advanced its STOMP simulator in a number of technical aspects; transitioning from equilibrium to kinetic formulations, from single-component to compositional hydrates, and from structurally static to geomechanically dynamic. Recognizing this aspect of the numerical simulation by the NETL program managers, Richard Baker and Ray Boswell, has helped to realize the current state of computational and analytical tools for gas hydrates at the national laboratories. PNNL greatly appreciates the vision, understanding and support of these program managers.

Acronyms and Abbreviations

AGU	American Geophysical Union
BP	Budget Period
ECKEChem	Equilibrium, Conservation, Kinetic Equation Chemistry
EDX	Energy Data eXchange
KE	Kinetic Exchange
KIGAM	Korea Institute for Geoscience and Mineral Resources
HYD	Binary Hydrate
HYDT	Ternary Hydrate
IGHCCS	International Gas Hydrate Code Comparison Study
JOGMEC	Japan Oil, Gas, and Metals National Corporation
LBNL	Lawrence Berkeley National Laboratory
NETL	National Energy Technology Laboratory
PNNL	Pacific Northwest National Laboratory
RGA	Residual Gas Analyzer
STOMP	Subsurface Transport Over Multiple Phases
T+H	TOUGH plus Hydrate
THC	Thermal, Hydrologic, Chemical
THM	Thermal, Hydrologic, Mechanical
UBGH	Ulleung Basin Gas Hydrate
XRD	X-Ray Diffraction

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1.0 Introduction

Numerical simulation and laboratory experimental capabilities for conducting gas hydrate research at PNNL had previously been supported by NETL. This section provides an overview of the state of those capabilities and statements of the potential impact of research at the start of this project.

1.1 State of Research Capabilities at the Project Start

Numerical simulation capabilities for producing natural gas hydrates from geologic reservoirs have generally been directed at conventional technologies: depressurization, thermal stimulation, and inhibitor injection. For these conventional technologies hydrates of natural gas dissociate in response to thermodynamic conditions being shifted outside of the hydrate stability zone. An international collection of numerical simulators with capabilities for modeling conventional technologies for producing natural gas hydrates were demonstrated and compared in a DOE NETL sponsored gas hydrate code comparison project (Wilder et al., 2008). An attractive unconventional technology for producing natural gas hydrates is the guest-molecule-exchange approach, where the methane guest molecule is replaced with a thermodynamically favored gas molecule, without significantly altering the clathrate structure. Carbon dioxide and nitrogen are molecules currently under consideration for this technology in the production of natural gas hydrates.

To numerically simulate the guest-molecule-exchange technology conservation equations are required for all of the hydrate components, and equilibria formulations are required for mixed hydrates. Laboratory-scale experiments (Masuda et al., 2011) have additionally shown that the exchange of guest molecules is a kinetic process. Over the last six years the Korea Institute of Geoscience and Mineral Resources (KIGAM) has supported collaborative studies with the Pacific Northwest National Laboratory (PNNL) in developing, validating, and applying numerical simulation to the production of geologic accumulations of natural gas hydrates. Collaborative projects during this period have helped to realize three numerical simulators: 1) STOMP-HYD, an equilibrium based numerical simulator for binary hydrate systems; 2) STOMP-HYD-KE, a kinetic based numerical simulator for binary hydrate systems; and 3) STOMP-HYDT-KE, a kinetic based numerical simulator for ternary hydrate systems. The STOMP-HYDT-KE simulator will be used for the numerical components of this work.

STOMP-HYDT-KE has capabilities for modeling the production of natural gas hydrates via depressurization, thermal stimulation, inhibitor injection, and guest molecule exchange. The “HYDT” in the simulator name indicates that it considers the ternary hydrate system $\text{CH}_4\text{-CO}_2\text{-N}_2$, and the “KE” in the simulator name indicates that the exchange of guest molecules and formation/dissociation of gas hydrates is modeled as a kinetic process. One of the biggest obstacles to the development of STOMP-HYDT-KE was devising an equation of state that was reasonably accurate, computationally efficient, and free of convergence failures. The $\text{CH}_4\text{-CO}_2\text{-N}_2$ system is particularly difficult to resolve in the hydrate stability region, as the mixture is often near its critical point. A hybrid tabular-cubic equation of state was developed that overcame convergence issues associated with pure cubic equations of state near the mixture critical point. The hybrid scheme uses tabular data and an innovative interpolation algorithm to establish the existing phases, gas molar fractions, and phase compositions. The cubic equation of state is then used to calculate phase densities and fugacity coefficients. STOMP-HYDT-KE is currently being benchmarked and has been successfully applied to an experiment conducted at the Korea Institute for Geoscience and Mineral Resources (KIGAM) involving the injection of a $\text{CO}_2\text{-N}_2$ mixture into a CH_4 hydrate bearing, unsaturated column of sand.

Before large scale commercial recovery of natural gas from hydrates can be attempted, important issues regarding reservoir stimulation techniques, safety, and cost must be addressed. Reservoir modeling is an important tool that can be utilized to help address these issues. However, application of these modeling

tools requires access to reliable thermodynamic, kinetic, and physical property data for gas hydrates and physicochemical properties of the hydrate bearing sediments themselves. Laboratory studies conducted on synthetic gas hydrate sands have included characterization of gas chemistries with a residual gas analyzer. In the past, the gas composition on a synthetically rich methane hydrate core was successfully monitored, which allowed use to obtain hydrate dissociation kinetics. The planned experiments take advantage of the previous experiments. Furthermore, measurements planned for the pressurized XRD technique are unique and would have been some of the first reported. This technique was successfully used to track mineral dissolution, carbonation reactions, and mineral volume changes. The types of structural information gained from this technique are believed to improve the fundamental understanding of mechanisms occurring during the gas swapping process.

1.2 Potential Impacts of the Research at the Project Start

The conventional technologies for producing natural gas hydrates from geologic repositories, especially those with pore-filling type hydrates is reasonably well understood, and numerical simulations have been compared against field trials (Kurihara et al. 2008). In contrast, the guest-molecule-exchange approach for natural gas hydrate production is emerging unconventional technology. Laboratory-scale experiments by ConocoPhillips and the University of Bergen, Norway had demonstrated the exchange of CO₂ with clathrated CH₄, but there have only been a limited number of numerical simulation investigations of the technology. This project provided an opportunity for a recently developed numerical simulator, STOMP-HYDT-KE, to be used to aid in the interpretation of the data collected from the 2012 Ignik Sikumi gas hydrate field trial. The ultimate objective for this field of research was to develop numerical simulation tools with the capabilities of predicting the performance of the guest-molecule-exchange technology at the reservoir scale, including the geomechanical stability of the process. The work represents a first step in validating a numerical simulator with capabilities for modeling the kinetic exchange of hydrate guest molecules. A credible interpretation of the Ignik Sikumi gas hydrate field trial, realized through numerical simulation, would greatly aid in the understanding of the fundamental exchange processes for hydrate formers.

The purpose of the experimental work reported here was to conduct key laboratory studies with synthetic methane hydrate rich sand representative of Bentheim sandstone to obtain kinetic exchange rates for exchanging CO₂/N₂ with CH₄. Experimental results reported, recently to the start of this project, by Ersland et al. (2010) indicate the process of CO₂-CH₄ exchange occurs without destroying the hydrate structure. Their experiments utilized liquid CO₂, whereas, the current approach relies on a mixture of CO₂/N₂ that will be exchanged for CH₄. By conducting these short-term experiments, the proposed experimental techniques can identify optimized conditions for the mixed gas exchange process. The goal of this experimental work was to conduct necessary measurements of methane hydrate dissociation and structural stability in hydrate-bearing sediments using a high-pressure cell and state-of-the-art analytical techniques. The kinetic exchange rates obtained on the ternary gas system were then to be utilized to validate numerical codes and the structural data further support the concept of continuous stability of gas hydrate structures during gas swapping.

2.0 Budget Period 1

Budget Period 1 (BP1) spanned FY2013 and FY2014 and involved both experimental and numerical tasks. This first budget period was initiated with a meeting at the ConocoPhillips headquarters in Houston, Texas, where, ConocoPhillips presented a review of the Ignik Sikumi gas hydrate field trial, and formally released a report on the experiment. ConocoPhillips additionally announced, during this meeting, the exit of the company from its natural gas hydrates research and development programs. During BP1, PNNL conducted complementary research for the Korea Institute of Geoscience and Mineral Resources (KIGAM). This research was solely numerical in nature and investigated three production approaches for producing suboceanic accumulations of natural gas hydrates at the UBGH2-6 Site within the Ulleung Basin of the Korean East Sea: 1) single-well depressurization, 2) single-well injection of flue gas and subsequent moderate depressurization production, and 3) 40-acre five spot pattern of flue gas injectors and moderate depressurization producers. The total PNNL budget for BP1 was \$90,000.

2.1 BP1 Objectives and Scope

During BP1, this project was focused on the kinetics of exchanging CO₂ and N₂ with clathrated CH₄ in hydrate bearing geologic media. The project comprised two distinct components: 1) numerical investigation of the 2012 Ignik Sikumi gas hydrate field trial, and 2) experimental investigation of kinetic exchange processes in laboratory-scale hydrate bearing unconsolidated sands. The principal objective of the numerical component was to provide an interpretation of the data gathered at Ignik Sikumi Well #1. The experiment component of this project was designed to provide kinetic exchange parameters needed in the numerical simulation. The principal objective of the two experiments was to provide an order of magnitude value to the kinetic exchange parameters for the field-scale simulations of the Ignik Sikumi gas hydrate field trial.

2.1.1 Ignik Sikumi Investigations and Modeling

Data collected during the Ignik Sikumi gas hydrate field trial was extensive and well documented. A clear interpretation of the data, however, required an understanding of the fundamental subsurface processes coupled with the not well understood processes of hydrate former exchange, secondary hydrate formation, and primary hydrate dissociation. It was not anticipated that the funding level provided during BP1 would be sufficient to complete the planned numerical and experimental work, and that the work would be completed under BP2. Over BP1 and BP2, this project progressively developed, through comparison of numerical simulation results against the collected field trial data, an interpretation of the Ignik Sikumi gas hydrate field trial. The scope of the project was to determine the geologic models and mathematical processes models that provided an interpretation of field trial and provided agreement with the diverse variety of collected data (e.g., cumulative produced water, differential recoveries of N₂ and CO₂, temperature histories, produced sand). An additional focus of this project was to investigate the fate of the CO₂ and N₂ mixture during the injection period. Among the unknowns from the field trial were the roles of the non-hydrate-bearing layers above and below the target horizon.

Field data from the 2012 Ignik Sikumi gas hydrate field trial was made available in February 2013 (<http://prod-mmedia.netl.doe.gov/requestData.php>). The field trial, a collaborative project among the U.S. DOE NETL, ConocoPhillips Company, and Japan Oil, Gas, and Metals National Corporation (JOGMEC), investigated the injectivity of 210,00 scf of a CO₂/N₂ gas mixture into a hydrate-bearing horizon on the Alaska North Slope and then flowback of gas at pressures above and below the hydrate stability limit. A review of the released data was made during March 2013 meeting at ConocoPhillips Company headquarters in Houston, Texas. One outcome from this meeting is that the data do not readily allow a full interpretation of subsurface processes that occurred during the trial. With this research we

planned to use data from the field trial to serve as observations against which to compare numerical simulation results from STOMP-HYDT-KE.

The numerical investigations, by PNNL, during BP1 was an attempt to reproduce the observed responses during the injection, soak, and production stages of the test conducted at Ignik Sikumi #1 well. Numerical simulations were executed with the newly developed STOMP-HYDT-KE simulator with capabilities for modeling the kinetic exchange of three sl hydrate formers (i.e., CH₄, CO₂, and N₂). The simulations were directed at understanding the fate of the injected gaseous mixtures of CO₂ and N₂, the potential exchange of hydrate formers during the soak period, and the recovery ratios of produced CO₂ and N₂.

2.1.2 Laboratory Experiments for Kinetic Parameter Determinations

The original plan for the laboratory experiments involved two experimental scopes, both involving the exchange of gas hydrate guest molecules, one a flowing column experiment and the other a pressurized x-ray diffraction study. After working with the flowing column experiment, the scope of the project during BP1 was altered and the x-ray diffraction experiments were put on indefinite hold. For reference, this section describes the original laboratory objectives and scope.

PNNL planned to conduct a laboratory-scale experiment that involves three stages: 1) the production of CH₄ hydrate in sandstone, 2) replacement of the core gas with a mixture of CO₂ and N₂ at the Ignik Sikumi gas hydrate field trial concentrations, 3) the monitoring of the core gas chemistry over time. Results were to be converted into kinetic exchange rates and parameters for use in the simulations conducted under the Ignik Sikumi History Match task. The fundamental concept of this planned experiment was to develop a standardized procedure utilizing a residual gas analyzer (RGA) for *in situ* characterization of pore gas before, during, and after the exchange of CO₂/N₂ for CH₄. PNNL planned on using columns constructed from HYDEX that were semi-transparent and allowed visual observation of the packed sand before and after hydrate formation. A multi-port thermocouple inserted into the center of the column allowed for *in situ* temperature tracking. Sized fractioned silica sand or silica beads were to be moistened with a measurable amount of water to produce a desired porosity of 30 to 40%. The reactor was to be submerged in a circulating chiller and pressurized with CH₄ to obtain a homogenized mixture of sand and methane gas hydrate. Hydrate formation was to be confirmed through changes in temperature and through visual observations.

The gas exchange was planned to begin by flushing the reactor with pre-determined mixtures of N₂ and CO₂. Discrete gas samples were to be collected and analyzed by the residual gas analyzer to obtain values for the partial pressures of CO₂, N₂, and CH₄. The values obtained from the RGA were to allow tracking of the CH₄ swapping with CO₂/N₂ over a specific period of time. A final measurement was to also be taken after the temperature was increased above the hydrate stability zone, which would release any remaining CH₄ hydrate. Results from this scoping experiment were to provide quantitative estimates for the original amount of CH₄, the exchanged concentration of CO₂/N₂, and the presence of residual CH₄ hydrate.

PNNL planned to conduct a laboratory-scale experiment that involved three stages: 1) the production of CH₄ hydrate in sandstone, 2) replacement of the core gas with a mixture of CO₂ and N₂ at the Ignik Sikumi gas hydrate field trial concentrations, 3) the monitoring the gas hydrate structure. The results from this experiment were to contribute to the validation of the conceptual model for the guest-molecule-exchange process; where, a principal assumption was that large-scale dissociation of the hydrate did not occur during the process.

Pressurized XRD experiments were to be conducted in a Bruker-AXS Discover 8 x-ray diffraction unit equipped with a custom-built temperature stage (-110° to 225°C), rotating Cu anode (18,000 watts), and a

real time 2-dimensional area detector. The instrument, designed to analyze gas hydrate samples under reservoir conditions, was to use x-ray transparent high-pressure beryllium cells, as shown in Figure 2.1. The bottom portion of the cell and the insert are all composed of stainless steel or aluminum. A small window on the sample cup is either beryllium or Kapton. Rubber gaskets are used to seal between the beryllium pressure cap and the base. Pressurization is accomplished through the bottom of the cell.

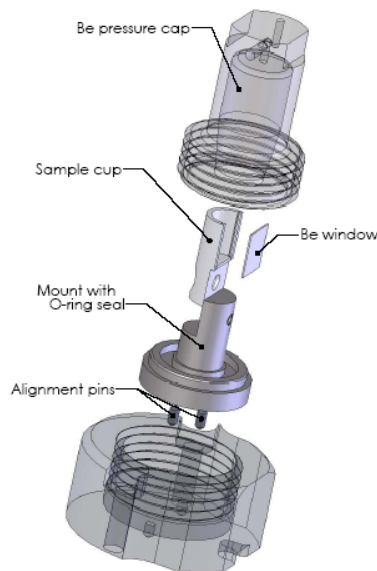


Figure 2.1. High-pressure XRD beryllium cell with internal sample cup.

Methane hydrate was to be synthesized by adding moist quartz sand to the sample cup and pressurizing with CH_4 to ~ 1000 psi after lowering the temperature to -2°C . After maintaining these conditions for several hours, XRD was to be collected until analyses reveal water ice formation. The primary reflections associated with water ice, detailed in PDF # 16-0687, were considered to be easily detected. Increasing the cell temperature to 1°C should destroy water ice and produce methane gas hydrate, which would produce distinctly different reflections. Powdered diffraction data for a structure I (sI) methane hydrate provided by (Bertie and Jacobs, 1982) included reflections at 25.99° ($I=35\%$), 27.08° ($I=55\%$), and 28.12° 2θ ($I=100\%$). The presence of sII clathrate hydrate in a sample was difficult to ascertain due to similar diffraction tracings between the sI and sII clathrate hydrates. Reflections produced by the beryllium cell are positioned at high 2-theta values and should not have interfered with the analysis.

Swapping of the methane with CO_2/N_2 was to take place simply by sweeping out the residual CH_4 while the reactor was still mounted on the XRD unit. Continuous monitoring of the hydrate structure was to be easily obtained while holding the cell pressure and temperature constant. If quartz sand was used, the primary reflection (26.64° 2θ) could be utilized as an internal standard if needed. Gas chemistry was to also be obtained with the RGA to verify the existence of CH_4 after the swapping had occurred. Finally, the cell temperature could be increased above the hydrate stability field and another gas sample collected to verify the existence residual CH_4 hydrate. The final results of this experiment were planned to provide further evidence of a continuous gas hydrate structure during gas swapping. Additional experiments could have been initiated with different CO_2/N_2 ratios to obtain a broader understanding of the gas hydrate structure under these conditions.

2.2 BP1 Accomplishments

On the numerical side of the project, there were four principal objectives during BP1: 1) review archived data and previous simulation attempts, 2) execute simulations of the Ignik Sikumi gas hydrate field trial, 3) compare simulation results against those from other modeling groups, and 4) report on the interpretations. At the start of this project, the STOMP-HYDT-KE simulator was nearing the end of its development stage and had been demonstrated against laboratory-scale experiments, conducted at KIGAM. The simulator, however, had not been applied beyond that verification exercise. The initial activity of this project was to review the numerical solution scheme and algorithms of the STOMP-HYDT-KE simulator. This review prompted a moderate redesign of the phase conditions, flash algorithms, boundary conditions, initial conditions and sources. The phase conditions were collapsed to four core conditions with options within each core condition: 1) aqueous saturated without hydrate, 2) aqueous unsaturated without hydrate, 3) aqueous unsaturated with hydrate, and 4) aqueous saturated with hydrate. The boundary conditions were collapsed to energy and flow types, and the number of initial condition variable options was reduced. All of the elements of the code redesign have been implemented and verified for proper execution.

On the experimental side of the project, there were two principal objectives during BP1: 1) conduct a guest molecule exchange experiment involving the injection of gas mixtures of N_2 and CO_2 into a CH_4 hydrate bearing sediment, and 2) exchange N_2 and CO_2 with CH_4 hydrates, while continuously monitoring the gas hydrate structure via a specially designed pressurized x-ray diffraction capability.

2.2.1 Accomplishments against Ignik Sikumi Investigations and Modeling

The STOMP-HYDT-KE simulator was applied to the Ignik Sikumi field trial with the objective of using numerical simulation to interpret the collected data from the field trial. Simulations were conducted over three periods of the field trial: 1) injection, 2) soak, and 3) production. This simulation work was documented in two papers (White et al., 2014; Anderson et al., 2014). Numerical simulation of the injection period of the Ignik Sikumi #1 field trial revealed three important processes. The guest molecule exchange process alters the equilibrium state for the hydrate, which can lead to hydrate dissociation or secondary hydrate formation. The guest molecule exchange process additionally alters the density of the hydrate, which can change the effective exchange process from being a one-to-one molar exchange. The concept of bound-water is critical to preventing secondary hydrate from forming and clogging the pore space. Comparison of the numerical simulations against the data collected during the injection period of the Ignik Sikumi #1 field trial is not sufficient for uniquely determining the kinetic rate parameters for hydrate formation, dissociation, or guest-molecule exchange, as agreement between the gas injection rates between the field trial and numerical simulations can be made with different kinetic parameters by moderate alterations in scaling of the reservoir intrinsic permeabilities.

2.2.2 Accomplishments against Laboratory Experiments for Kinetic Parameter Determinations

A series of guest-molecule exchange experiments have been conducted involving the replacement of mixtures of N_2 and CO_2 with clathrated CH_4 under different temperature and pressure conditions. The target pressure and temperature conditions varied between being within and outside the stability zone for the N_2 and CO_2 mixture, but always within the stability zone for pure CH_4 hydrate. The first study targeted under this task was the development of a standardized procedure to perform in situ monitoring of pore gas chemistry during the replacement of methane in a CH_4 hydrate bearing porous sand with CO_2 through the titration of a gaseous mixtures consisting of different ratios of N_2/CO_2 . The continuous monitoring of pore gas chemistry would provide clear evidence of the rates associated with the exchange of CH_4 with CO_2 . The experimental procedure involves three main stages: 1) the formation of CH_4

hydrate in a porous sandstone, 2) replacement of the core gas with a N_2/CO_2 gas mixture, and 3) the monitoring of the core gas chemistry over time during the exchange process. The goal of these scoping experiments is to develop kinetic exchange rates and parameters for use in the simulations conducted under the Ignik Sikumi History Match task.

For the initial test, fine-grained silica sand (20-40 mesh; 0.4-0.5 mm) was moistened with de-ionized water to 9% saturation and compacted to 0.42 porosity in a cylindrical, semi-transparent HYDEX column (1.9 cm inner diameter; 20.4 cm length) equipped with a thermocouple inserted in the center of the column. The column was sealed, wrapped with copper tubing, and cooled to $+2^\circ C$ by circulating chilled fluid through the tubing. The column was then pressurized to 1,000 psi with CH_4 and cooled to $-2^\circ C$, and subsequently cycled between $+2^\circ$ and $-2^\circ C$ for several days to promote hydrate growth. Initially hydrate formation was confirmed through changes in temperature and over time, through visual observations of a white fine-grained material appearing in the pore spaces.

The exchange experiment was conducted while the column was maintained at $2^\circ C$ and ~ 1000 psi. Using the ISCO syringe pump, a gas mixture consisting of 90% N_2 and 10% CO_2 was titrated into the bottom of the column and allowed to flow out through the top at 0.5 mL/min. Constant flow was maintained by utilizing a finely tuned pressure relief valve at the outlet (top of column) as well as a by-pass valve. A continuous gas sample was collected from the outlet and passed directly into the RGA where partial pressures for masses corresponding to CH_4 (16), CO_2 (44), and N_2 (28) were monitored. The values obtained from the RGA are shown in Figure 1 and illustrate the evolution of the pore gas chemistry over time. Initially, before the start of the titration, CH_4 has the highest partial pressure. However, shortly after introducing the N_2/CO_2 gas mixture, the N_2 partial pressure began a steady increase and the CH_4 partial pressure declined. This is an expected trend and indicates the changing concentrations of CH_4 and N_2 in the column. Concentrations of CO_2 , monitored through observing the partial pressure of mass 44 (CO_2), remain constant for the first 2.2 hours before showing signs of an increase. Increasing CO_2 concentrations occurred until about 6 hours in to the titration, after which they remained relatively constant. After 20 hours, the column was isolated, and the temperature increased above the hydrate stability zone ($\sim 18^\circ C$) to allow all the existing hydrate to disassociate. The final gas analysis showed ~ 3 times the amount of CO_2 to CH_4 , which indicates a significant amount of CO_2 hydrate existed in the column. Staff repeated this experiment with the addition of a flushing step to remove any free CH_4 in the column prior to disassociating the hydrate. Funding for the x-ray diffraction experiments was diverted to further the guest-molecule exchange experiments because of the value of the collected kinetic data.

To observe the hydrate distribution in the core, improvements were made to the experimental apparatus. Eight new thermocouple sensors have been added that span the column and allow us to observe the temperature distribution. This addition led to the implementation of custom-built foam cooler which insulates the experimental column. A pressure transducer has also been added to the outlet in order to allow for more accurate measurements of the pressure conditions across the core. While the procedure remains largely the same, the method to form the initial methane hydrate has evolved. Current experiments allow time for the methane to fully saturate the aqueous phase prior to lowering the temperature and raising the pressure. Additionally, the sand packed column is now horizontally aligned, in order to reduce the effects of gravity on flow through the column. The fine-grained silica sand (20-40 mesh; 0.4-0.5 mm) that has been used for all experiments was replaced with a finer-grained "Accusand", due to non-uniform initial aqueous saturations.

A flow-through CH_4 replacement experiment was performed in a sand column at conditions similar to those at Ignik Sikumi #1 to collect and validate hydrate formation and exchange parameters (s_{lb} , K_f , $K_{e,f}$) used in the development of the STOMP-HYDT-KE model. The experiment was performed in three phases: 1) hydrate formation for 40 hours, 2) guest molecule exchange with 77.5/22.5 N_2/CO_2 molar ratio at 0.38 ml/min titration for 100 hours, 3) rapid gas vacuum and thermal dissociation for 18 hours. Data were collected through a residual gas analyzer (RGA), an inlet flow syringe pump, an outlet pressure transducer and eight temperature probes across the column.

The experiment was conducted using a custom built cylindrical, semi-transparent HYDEX column (1.9 cm inner diameter; 20.4 cm length) equipped with a custom built 8-point thermocouple (OMEGA Engineering Inc.) inserted in the center of the column (Fig. 2.1). The thermocouple was designed with a single probe hosting eight temperature sensors set with 2.5 cm spacing across the length of the column. Column pressures were monitored using a 1,500-psi pressure transducer (PX409-USBH Series, OMEGA Engineering Inc.) attached to the downstream end of the outlet port. The assembled column was sealed, wrapped with copper tubing and placed horizontally in a custom-built foam cooler. The column was then pressurized at room temperature to 1,215 psi with CH₄ and allowed to equilibrate for a sufficient time for the methane to fully saturate the aqueous phase. The cooler was then packed with ice and the column temperature was cooled to ~2°C by circulating chilled fluid through the copper tubing.

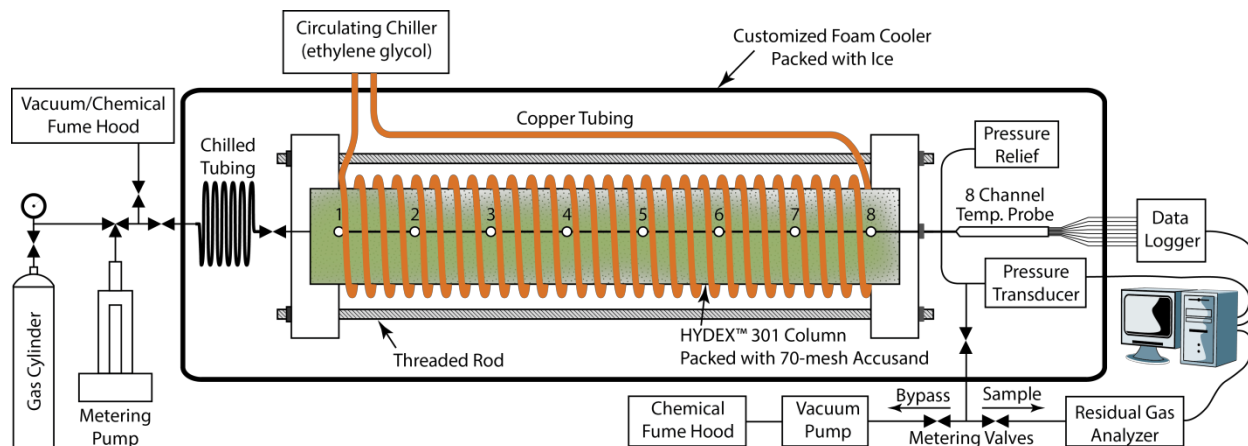


Figure 2.2. Flow-through experimental apparatus

3.0 Budget Period 2

Budget Period 2 (BP2) spanned FY2014 and FY2015 and was limited to numerical simulation tasks. The total PNNL budget for BP2 was \$80,000.

3.1 BP2 Objectives and Scope

During BP2, this project continued and expanded the investigations of BP1. Numerical simulations of the 2012 Ignik Sikumi gas hydrate field trial were continued to resolve disagreements between simulation results and field trial observations, and to provide a more thorough interpretation of the field results. Simulation results generated during BP1 used a single geologic model to represent the hydrate reservoir surrounding the Ignik Sikumi #1 well. One objective of the history match study during BP1 was to investigate whether it was possible to reproduce the field trial results with the available characterization data collected. The objective of this subtask was to investigate whether there are geologic factors that could yield closer agreement between the numerical simulations and field trial observations. This investigation considered alternative realizations of the geologic model that honor the characterization data. Simulations of the Ignik Sikumi gas hydrate field trial was then repeated with the new geologic models and simulation results compared against the field observations and simulation results from other geologic model realizations.

During BP1 simulations were conducted using porosity, intrinsic permeability, and effective permeability based on the collected characterization data and calibrated to the observed injectivity. Other petrophysical properties, such as the k-s-P functions, thermal conductivity models and effective permeability as a function of ice and hydrate formation, used values typical for Alaska North Slope sandstones beneath the permafrost. This investigation, first, derived or created more specific models for the more generic functions, and then, second, explored the impact of using different parameters on the agreement between numerical simulation results and the field trial observations. A sensitivity study was conducted across the parameter and model space to determine which parameters and models had significant impact on comparison with the field observations. One outcome from the simulations conducted in the first budget period was that the numerical simulations predicted ice formation near the well, yielding pore plugging and loss of gas production during the depressurization stages. Temperatures taken during the field trials did not indicate the potential for ice formation. One of the first challenges for this budget period was to investigate this discrepancy between the simulation results and field observations. One remaining uncertainty was the role of the low hydrate layers above and below the target horizon.

The kinetic models used during the numerical simulations of BP1 considered the kinetics of hydrate formation, dissociation, and guest molecule exchange. All of these kinetic models used functional forms with constant hydrate surface areas. The kinetic models used during this budget period addressed changes in effective kinetic rates with changes in hydrate surface area. The numerical simulations in BP1 only explored a limited region of the kinetic parameter space. The numerical simulation results generated during BP1 did indicate differential amounts of N₂ and CO₂ produced as observed in the field trial, but the ratios were closer than those of the field trial. One objective for BP2 was to better understand the factors and mechanisms that contribute to the differences in recovered hydrate formers.

3.2 BP2 Accomplishments

In 2012 the U.S. DOE/NETL, ConocoPhillips Company, and Japan Oil, Gas and Metals National Corporation jointly sponsored the first field trial of injecting a mixture of N₂-CO₂ into a CH₄-hydrate bearing formation beneath the permafrost on the Alaska North Slope. Known as the Ignik Sikumi #1 Gas

Hydrate Field Trial, this experiment involved three stages: 1) the injection of a N_2 - CO_2 mixture into a targeted hydrate-bearing layer, 2) a 4-day pressurized soaking period, and 3) a sustained depressurization and fluid production period. Data collected during the three stages of the field trial were made available after a thorough quality check. The Ignik Sikumi #1 data set was extensive but contained no direct evidence of the guest-molecule exchange process. During BP2 numerical simulation was used to provide an interpretation of the $CH_4/CO_2/N_2$ guest molecule exchange process that occurred at Ignik Sikumi #1. Simulations were further informed by experimental observations. The goal of the scoping experiments was to understand kinetic exchange rates and develop parameters for use in Ignik Sikumi history match simulations. The experimental procedure involves two main stages: 1) the formation of CH_4 hydrate in a consolidated sand column at 750 psi and $2^\circ C$ and 2) flow-through of a 77.5/22.5 N_2/CO_2 molar ratio gas mixture across the column. Experiments were run both above and below the hydrate stability zone in order to observe exchange behavior across varying conditions. The numerical simulator, STOMP-HYDT-KE, was then used to match experimental results, specifically fitting kinetic behavior. Once this behavior is understood, it can be applied to field scale models based on Ignik Sikumi #1. A poster documenting this work was presented at the 2015 AGU Fall Meeting (Ruprecht et al., 2015).

The principal objective of the numerical simulations is to provide an interpretation of the data collected from the Ignik Sikumi field trial, keeping the geologic and numerical models as simple as possible. A preliminary suite of numerical simulations was executed to calibrate the permeability parameters from the ConocoPhillips report (Schoderbeck et al., 2013) to the injected mass during the field trial. These simulations included both isotropic and anisotropic ratios of vertical to horizontal intrinsic permeability. The results from these simulations indicated good agreement between the simulations and field-trial data occurred using a vertical to horizontal anisotropy ratio of 0.1 and by scaling the intrinsic permeabilities by a factor of 1.5 from the ConocoPhillips report (Schoderbeck et al., 2013). A suite of injection simulations was executed that differed in the kinetic exchange rate constant, kinetic hydrate dissociation constant, kinetic hydrate formation constant, and ice pore clogging model. A typical plot of cumulative injected mass versus time shows a near-linear injection rate for both N_2 and CO_2 , with the total inject gas being 232.4 Mscf, compared with the field value of 215.9 Mscf. During the injection phase, there were only minor differences in the injected mass across the suite of simulations with varying kinetic parameters and ice pore clogging model.

The multifluid flow, phase transformation, and heat transfer processes occurring in the hydrate reservoir with the injection of N_2 and CO_2 are complex and strongly coupled. The state of the hydrate and gas saturations at the end of the injection phase (i.e., after 306 h) is shown in Figure 3.1, (left) and (right) respectively. The hydrate saturation vertical profile at the 20-m radial distance provides an indication of the initial hydrate saturation distribution via the strata. During the injection phase both primary hydrate dissociation and secondary hydrate formation occurred. The gas saturation profile is non-uniform due to the initial heterogeneities in the effective permeabilities and the changes in the hydrate saturation. Maximum migration of the gas into the reservoir is roughly 7 m from the center of the well. The state of the temperature at the end of the injection phase (i.e., after 306 h) is shown in Figure 3.2 (left). Near freezing conditions are predicted to occur in those regions where hydrate dissociation occurred and elevated temperatures are noted where the secondary hydrate formed, primarily in regions of lower initial hydrate saturations. It should be noted that the freezing temperature regions are not adjacent to the well casing, where the temperature of the injected gases helps to maintain the initial reservoir conditions. The region of increased gas pressure extends well beyond the gas saturation plume, which is typical for the injection of gases into saline formations.

The state of the N_2 , CO_2 , and CH_4 hydrate mole fraction of formers (i.e., ignoring hydrate water) at the end of the injection phase (i.e., after 306 h) is shown in Figure 3.2 (right), 3.3 (left) and (right), respectively. The exchange of guest molecules is primarily controlled by the concentration of injected N_2 and CO_2 , yielding hydrate with higher concentrations of N_2 . Deeper in the reservoir the hydrate is primarily a binary N_2 - CH_4 form, with the CO_2 being depleted in the region nearer to the well. Adjacent to the well are regions of CH_4 free hydrate that form with exposure of the hydrate to freshly injected N_2 and

CO₂, as shown in Figure 3.3 (right). Changes in the hydrate composition yield changes in the hydrate equilibrium pressure, with higher equilibrium pressures occurring in regions of higher temperatures and increased hydrate concentrations of N₂ and CO₂.

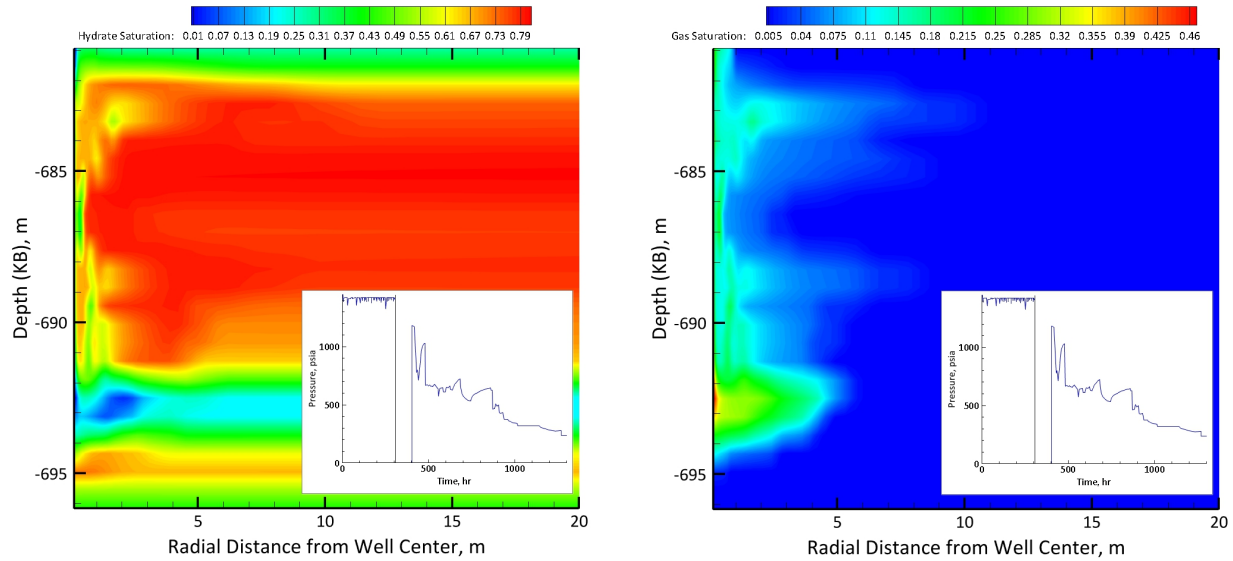


Figure 3.1. Hydrate (left) and gas (right) saturation at the end of the injection

A suite of simulations was conducted for all three phases of the Ignik Sikumi Field Trial. Six simulations from the suite are reported here, and principally vary in the guest-molecule exchange rate and the ice pore plugging model. The kinetic formation/dissociation constant used in Simulations #2 and #2c were roughly 10 times those used by Sun et al. (2005). The use of a bound-water saturation of 0.2 limits the formation and the rate of formation of hydrates. Injection of the N₂-CO₂ into the reservoir creates gas saturation around the injection well and yields a positive driving force for the exchange of N₂ and CO₂ with CH₄ in the hydrate. The rate of exchange is controlled by the kinetic exchange rate parameter and the difference in former vapor pressures and hydrate equilibrium partial pressures. As N₂ and CO₂ exchange with the CH₄ in the hydrate the hydrate composition shifts as does the hydrate equilibrium pressure, density, and enthalpy. The injection rates force the gas mixture deeper into the reservoir, transporting unexchanged N₂ and CO₂, and exchanged CH₄ away from the well.

Gas migration is controlled by the heterogeneity in the effective permeability of the strata and the heterogeneity that develops as hydrate dissociates and forms in response to the gas mixture injection. When the kinetic exchange rate constant is increased to 1.0×10^{-3} kmol/m³ a greater percentage of the injected N₂ and CO₂ becomes incorporated into hydrate rather than remaining in the mobile phases (i.e., aqueous and gas). An interesting result from these simulations is that there is a net increase in the hydrate mass, primarily due to the increase in hydrate density with the alteration in hydrate composition. The CH₄ rich hydrate has a density of around 915 kg/m³, whereas the N₂ and CO₂ rich hydrate has a density of around 1080 kg/m³. This shift in hydrate density alters the effective molar exchange ratio of guest-molecules to be more than 1 to 1.

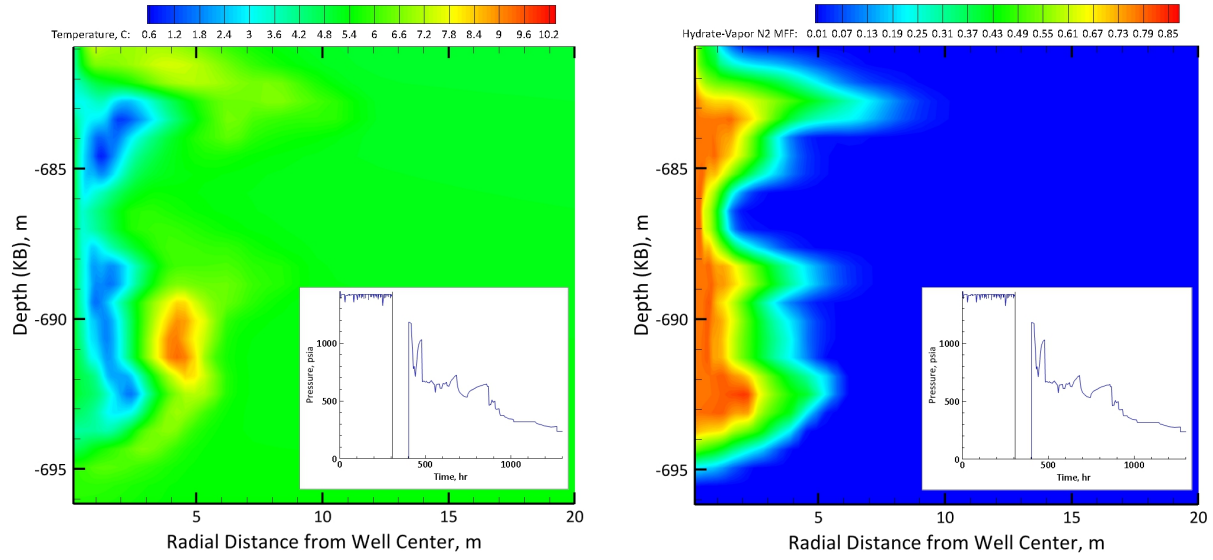


Figure 3.2. Temperature (left) and hydrate N₂ mass fraction of formers (right) at the end of the injection

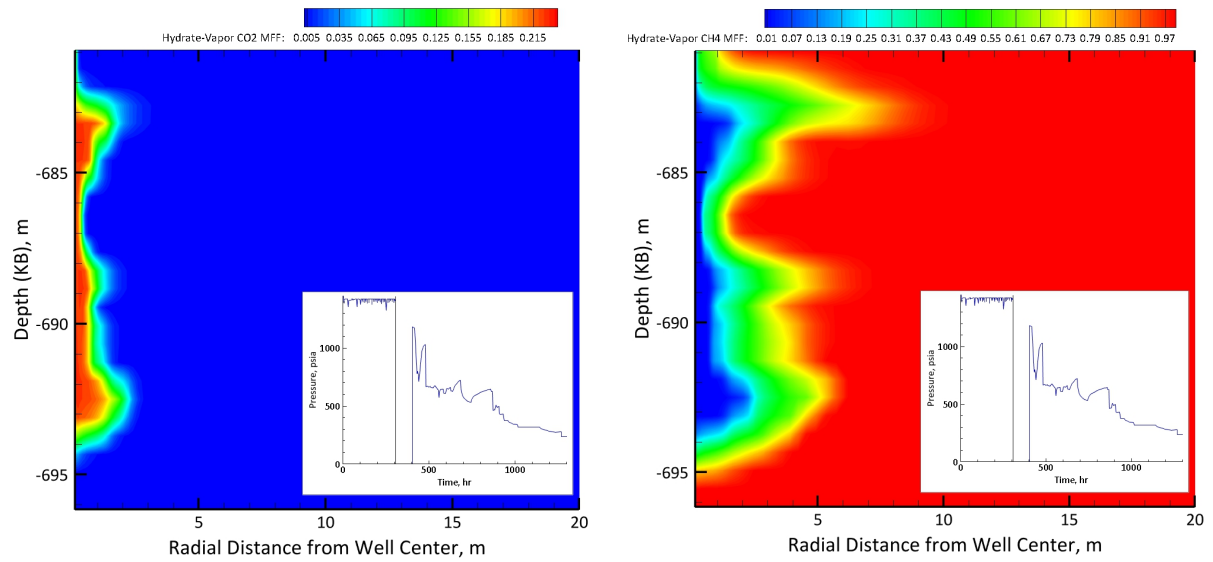


Figure 3.3. Hydrate CO₂ (left) and CH₄ (right) mass fraction of formers at the end of the injection

4.0 Budget Period 3

Budget Period 3 (BP3) spanned FY2015 and FY2016, was limited to numerical simulation tasks and was refocused from the guest-molecule exchange production technology to implementing geomechanics. The results of the Nankai Trough experiment (Qiu et al., 2014; and Yamamoto et al. 2014) indicated the critical importance of understanding the geomechanical processes in producing natural gas hydrates from suboceanic deposits. Numerical simulation studies of the geomechanical stability of hydrate-bearing sediments had previously been conducted via the coupling of two numerical simulators TOUGH+HYDRATE and FLAC3D (Rudqvist and Mordis, 2007). The TOUGH+HYDRATE simulator describes the hydraulic, thermal and thermodynamic behavior of hydrate-bearing geologic media, subjected to thermal, fluid pressure, and inhibitor concentrations that can induce hydrate dissociation or formation. The FLAC3D (Itasca, 2002) geomechanical simulator is widely used for rock mechanics problems and includes a variety of constitutive mechanical models that allow the simulation of quasi-static yield and failure, time-dependent creep, and more conventional elastic deformation. The two numerical simulators are externally linked through a thermal-hydrological-mechanical model; where the basic couplings between the two simulators are considered through: 1) an effective stress law, which relates changes in pore pressure and temperature affect mechanical deformation and stress, and 2) a pore-volume model that defines how changes stress or strain alter porosity and intrinsic permeability. At the start of BP3, none of the STOMP simulators, including STOMP-HYDT-KE, had capabilities for modeling geomechanical systems. The PNNL team considered following the external coupling approach taken by the Lawrence Berkeley National Laboratory team, but instead opted for developing a porothermoelastic capability from scratch, following the STOMP coding protocols. This became the principal objective of the BP3. The total PNNL budget for BP3 was \$50,000.

4.1 BP3 Objectives and Scope

The STOMP-HYDT-KE simulator is designed as a reservoir simulator for the production of natural gas hydrate from geologic accumulations, such as those which occur in suboceanic deposits and beneath the arctic permafrost. The simulator has capabilities for modeling a combination of production technologies, including conventional and nonconventional: 1) depressurization, 2) thermal stimulation, 3) inhibitor injection, and 4) guest-molecule exchange. The simulator has undergone a series of transitions involving stages of development and application, with each development being targeted at specific capability gap. For example, the original version of the simulator assumed equilibrium between the hydrate and mobile phases but failed reproduce experiments with non-equilibrium conditions. The next version resolved this with the implementation of a kinetic exchange formulation, but then was unable to simulate injection of N_2 - CO_2 mixtures. The current version considers ternary hydrates, with three mobile phases (i.e., aqueous, gas, and nonaqueous liquid), and kinetic exchange of formers between the hydrate and mobile phases. This would be considered to be coupled thermal, hydrologic, and chemical (THC) processes. The code additionally has geochemical modeling processes, via is ECKEChem reactive transport module, but is generally unused for hydrate production simulations. The results of the Nankai Trough experiment (Qiu et al., 2014; and Yamamoto et al. 2014) indicate the critical importance of understanding the geomechanical processes in producing natural gas hydrates from suboceanic deposits. During BP3, the project sought to develop coupled geomechanical simulation capabilities into STOMP-HYDT-KE simulator to allow the modeling of formation deformation with changes in the effective stress state, due to changes in temperature and pressure as a result of production activities.

Support from DOE NETL and KIGAM have yielded simulation capabilities in the STOMP-HYDT-KE simulator that allow for the modeling of fully coupled multifluid hydrologic, heat transfer, hydrate thermodynamics, and geochemistry. Moreover, the simulator is formulated to model the exchange of hydrate formers, hydrate dissociation, and hydrate formation as kinetic processes for a ternary hydrate former system N_2 , CO_2 , and CH_4 . The missing element in this suite of capabilities is the coupling with

4.2 BP3 Accomplishments

The diagram illustrates an 8-noded hexahedral element. The nodes are numbered 1 through 8. A global Cartesian coordinate system is shown on the left with axes x , y , and z . An element canonical coordinate system is defined by dashed lines with axes ξ , η , and μ . The grid-cell centroid is marked with a small circle. Nodal displacements at node 8 are labeled u_8 , v_8 , and w_8 .

Figure 4.4.1. Hexahedral-shaped finite element and finite-volume grid cell

The progress at the end of BP3 was principally in the development of a collection of subroutines that are called by the STOMP-HYDT-KE simulator. These subroutines are being collected into a single file called “geomech.F,” with the name of the file referring to its objective geomechanics. The first routines written were those to read geomechanical properties into elements. As the finite elements and finite-volume grid cells coincide this routine is similar to those for defining the petrophysical properties of the rocks. Currently the Geomechanical Properties Card reader routine allows input of the Young’s Modulus, Poisson’s Ratio, Biot Coefficient, and Thermal Expansion Coefficient. The next subroutine created was the numbering map for the finite-element nodes. Finite-element nodes are numbered, starting with the first node on the first element. All the nodes on the first element are numbered and that node number is transferred to all elements that share the node. Special consideration is given to splits in the domain, making certain to create unique nodes on either side of a split in the domain, such as might occur with displacement faults. Two utility routines were additionally written, one for transposing a matrix and one for multiplying two matrices.

The next suite of routines that have been developed are those for creating the stiffness matrix, which relates displacements with external and body forces on the domain. This suite of routines first computes the 24 x 24 elements of the stiffness matrix, which are loaded into the global stiffness matrix. This global stiffness matrix is order 3x the number of finite element nodes. The stiffness matrix is computed by multiplying the transpose of the strain displacement matrix (24 x 6) with the stress-strain matrix (6 x 6), with the strain displacement matrix (6 x 24), yielding the 24 x 24 stiffness matrix. A routine to compute the 6 x 24 components of the strain displacement matrix has been developed as a function of the location within the finite element in terms of the canonical coordinates, and the x-, y-, and z-coordinates of the node points. The element stiffness matrix is integrated over the finite element using Gauss integration. This routine has been developed such that the user can opt for 2, 3, 4, or 5 integration points in each direction. For the 2-point scheme 8 evaluations are required and for the 5-point scheme 125 evaluations are required.

The approach adopted to develop geomechanical capabilities for STOMP-HYDT-KE is more rigorous than coupling with external computer codes with these capabilities, but the resulting code is not reliant on this coupling. This provides greater flexibility in making future advancements, providing researchers with the power to test new numerical concepts and allow for greater computational performance. We anticipated that the code comparison activities being organized by NETL and LBNL as being focused on modeling THM systems for hydrate bearing formations and that this project would provide the needed geomechanical capabilities for STOMP-HYDT-KE to fully participate.

5.0 Budget Period 4

Budget Period 4 (BP4) spanned FY2016 and FY2017, was limited to numerical simulation tasks, coupled with a KIGAM funded project, and considered both geomechanics and the guest-molecule exchange production technology. The total PNNL budget for BP1 was \$50,000.

5.1 BP4 Objectives and Scope

A collaborative effort jointly-supported by DOE/NETL and the Korea Institute of Geoscience and Mineral Resources (KIGAM) was conducted in BP4. Building off of initial work in BP3 through DOE funding, KIGAM partially supported the continued development of coupled geomechanical simulation capabilities into STOMP-HYDT-KE simulator to allow the modeling of formation deformation with changes in the effective stress state, due to changes in temperature and pressure as a result of production activities. The target application for this development were natural gas hydrate production from the Suboceanic Gas Hydrate Deposits at the UBGH2-6 Site within the Ulleung Basin of the Korean East Sea. Also, in BP4 through DOE/NETL funding support, the project planned to compare simulation results against the swapping experiments previously conducted at KIGAM on hydrate bearing core samples.

The collaborative project had two scope topics: 1) developing fully integrated capabilities into STOMP-HYDT-KE for simulating the deformation of gas hydrate bearing reservoirs and overlying strata with changes in effective stress due to changes in pressure and temperature (KIGAM-funded); and 2) applying the STOMP-HYDT-KE against recent experiments conducted by KIGAM involving the swapping of gas mixtures of CO₂ and N₂ with CH₄ hydrate bearing core samples (DOE-funded). The geomechanical modeling capabilities were planned to be limited to linear elasticity, but also to include the ability to predict mechanical failure through a Mohr-Coulomb criterion. The funding levels for this project were considered to be insufficient to realize a fully validated and documented version of the geomechanics module, but demonstration of the capabilities was planned to be provided to KIGAM and DOE. Input file alterations associated with the geomechanics module were planned to be published in the dynamic user's guide on the STOMP website (stomp.pnnl.gov). Comparison of the STOMP-HYDT-KE simulator against the gas hydrate experiments conducted at KIGAM were planned to be limited to a jointly agreed suite of experiments.

PNNL planned to complete development of a geomechanical module initiated in BP3. This module was planned to be implemented into the STOMP-HYDT-KE simulator in a coupled, sequential scheme. When implemented coupled heat transfer, multifluid flow, and kinetic exchange of hydrate formers (coupled THC) would be solved using a global implicit solution scheme using a finite volume discretization with hexahedral grid cells. When this system is converged, the reactive transport module, ECKEChem, would be executed if geochemical reactions are required in the simulation of the natural gas hydrate production scenario. Following the geochemical calculations, the geomechanical calculations would be executed driven by changes in pressure and temperature computed from the coupled THC solution. The geomechanical module would yield stress, strain, and deformation at the nodal points of the finite-element grid, which would be comprised of six pyramidal elements that divide the coupled THC hexahedron grid. This task involved the development of a finite-element based linear elasticity geomechanical solver and implementation into the STOMP-HYDT-KE simulator using a coupled sequential overall solution scheme. The use of overlapping a structured hexahedron grid for the coupled THC solution and the pyramidal grid for the geomechanical solution eliminates the need for translation of the results between solutions.

PNNL planned to apply its STOMP-HYDT-KE simulator against experiments previously conducted at KIGAM involving the swapping of gas mixtures of CO₂ and N₂ with CH₄ hydrate bearing sample cores. The kinetic parameters determined from recent research conducted by PNNL (Yonkofski et al., 2016) was

planned to be used as initial values for these critical parameters. The principal objective of this research was to demonstrate the ability of the simulator to duplicate the experimental observations, and to identify needs in the understanding of fundamental processes. The governing equation framework of the STOMP-HYDT-KE simulator, with its independent tracking of mobile and hydrate components, provides options for explore fundamental processes and exchange mechanisms. PNNL worked with the scientists and engineers at KIGAM to develop input files that describe the KIGAM experiments, execute the needed numerical simulations, and the work with KIGAM to understand the simulation results against the experimental observations. The parameters determined for the kinetic parameters were based on comparisons against from experiments conducted at PNNL, published literature, and the Ignik Sikumi #1 Field Trial. Seeing these parameters work equally well for the KIGAM experiments would contribute to our confidence in understanding the fundamental processes, but conversely having the parameters not work is a valuable piece of scientific evidence about these processes.

5.2 BP4 Accomplishments

The two principal objectives of this project are the demonstration the STOMP-HYDT-KE simulator to model hydrate dissociation with nitrogen injection, and to model the geomechanical response of the system over the course of hydrate production and formation stabilization. The geomechanical capabilities in STOMP-HYDT-KE were partially developed during the KIGAM funded project, entitled “Geomechanics Implementation for the STOMP-HYDT-KE Simulator,” but not verified against analytical solutions. Before investigating the injection of nitrogen into natural gas hydrate bearing reservoirs, we sought to validate the geomechanics module, called GEOMech, against simple hydrothermogeomechanical problems with analytical solutions. One such problem is the Terzaghi Poroelastic Deformation problem (Verruijt, 2013). This one-dimensional deformation problem involves the compaction of fluid filled rock under a constant vertical stress. The stress plate is assumed to be highly permeable, allowing pressurized fluid to be expelled. As fluid leaves the system the rock compresses and a new equilibrium state is reached. A conceptualization of the Terzaghi problem is shown in Figure 5.1, taken from Verruijt (2013).

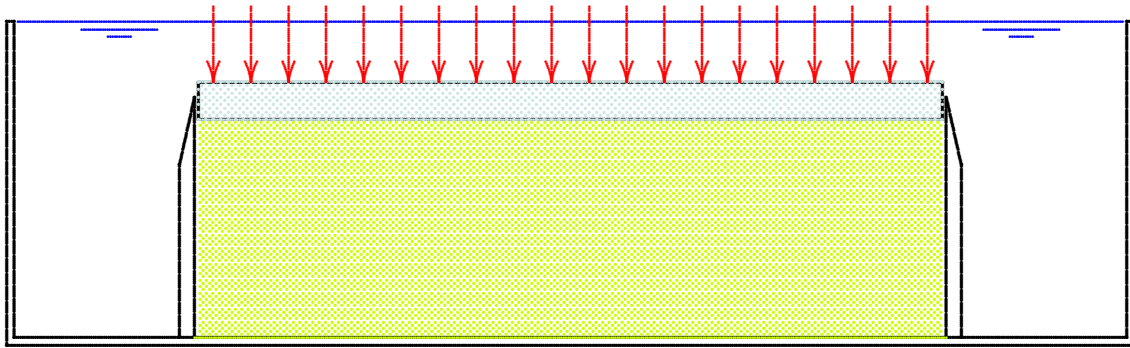


Figure 5.1. Conceptualization of the Terzaghi problem, taken from Verruijt (2013)

Verruijt (2013) published an analytical solution to the Terzaghi problem, which considered the compressibility of the rock particles and fluid. In Terzaghi’s original work the rock particles and fluid were assumed to be incompressible. The pressure solution published by Verruijt (2013) is

$$\frac{p}{p_0} = \frac{4}{\pi} \sum_{k=1}^{\infty} \frac{(-1)^{k-1}}{2k-1} \cos \left[(2k-1) \frac{\pi z}{2h} \right] \exp \left[-(2k-1)^2 \frac{\pi^2 c_v t}{4 h^2} \right]$$

where, p is the pore pressure, p_0 is the initial pore pressure, z is the height, h is the overall height, t is the time, and c_v is the consolidation coefficient, which is a function of the hydraulic conductivity, fluid density, storativity, Biot coefficient, and confined compressibility of the rock. The STOMP-HYDT-KE and GEOMech module were applied to the Terzaghi problem; where the coupled flow and transport, and geomechanics were solved in an iterative sequential fashion (i.e., coupled flow and transport then geomechanics). A fixed stress scheme was used for coupling flow and transport and geomechanics, with a convergence criterion set at 10^{-6} . A comparison of the STOMP-HYDT-KE simulation results and the Verruijt (2013) analytical solution is shown in Figure 5.2 for the pressure solution.

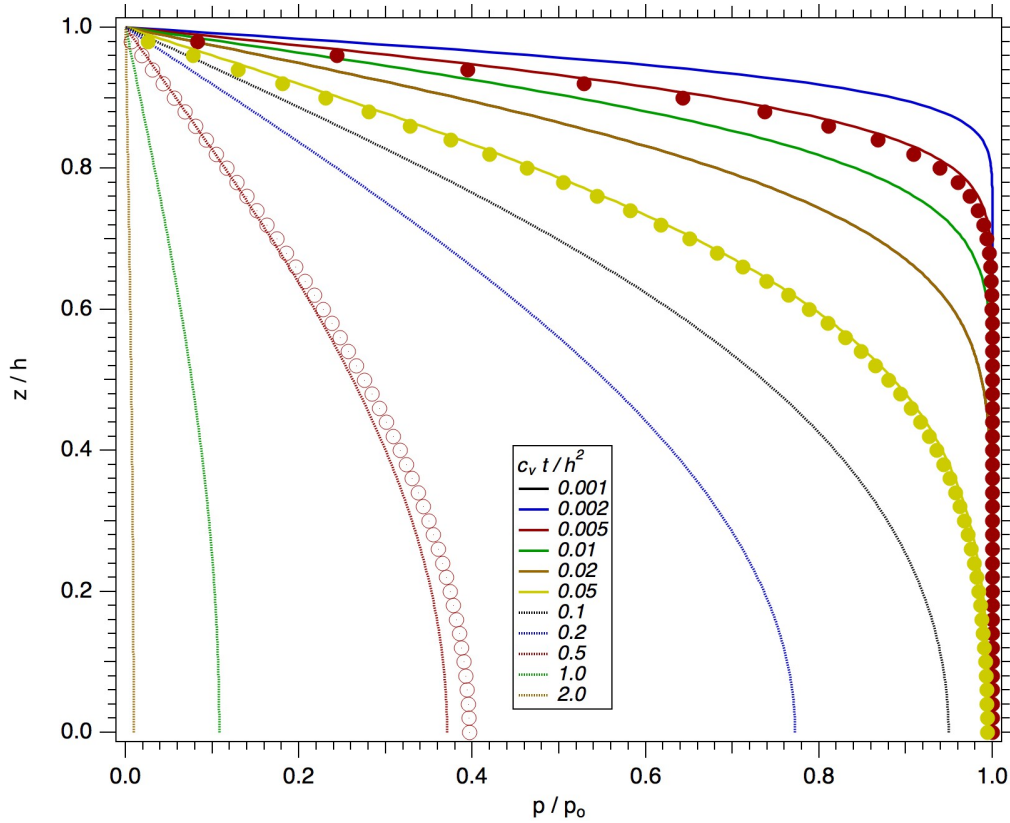


Figure 5.2. Pore pressure solution as a function of z/h and $c_v t/h^2$ with the analytical solution shown as lines and the STOMP-HYDT-KE solution shown as markers

Verruijt (2013) additionally provided an analytical solution for the deformation of the system. The displacement is described using a non-dimensional quantity, U , termed the degree of consolidation, defined as

$$U = \frac{w - w_0}{w_\infty - w_0}$$

where, w is the vertical displacement, w_∞ is the final vertical displacement, and w_0 is the initial vertical displacement. Verruijt's (2013) analytical solution for displacement is

$$U = 1 - \frac{8}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{(2k-1)^2} \exp \left[-(2k-1)^2 \frac{\pi^2 c_v t}{4 h^2} \right]$$

A comparison of the STOMP-HYDT-KE simulation results and the Verruijt (2013) analytical solution is shown in Figure 5.3 for the displacement solution. The comparisons between STOMP-HYDT-KE and the Verruijt analytical solutions for pore pressure and displacement, in Figures 5.2 and 5.3, shown good agreement. This indicates the coupled flow and transport and geomechanics scheme implemented in STOMP-HYDT-KE is working properly for one-dimensional poroelastic problems.

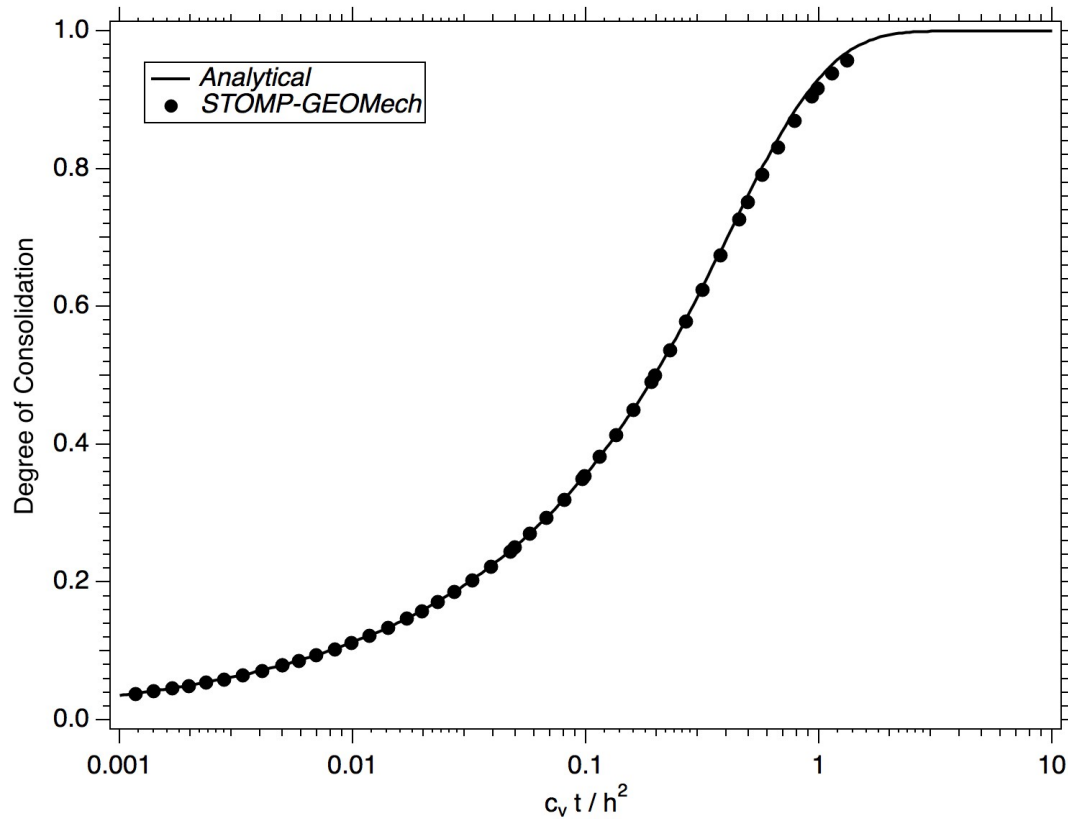


Figure 5.3. Degree of consolidation solution as a function of $c_v t / h^2$ with the analytical solution shown as lines and the STOMP-HYDT-KE solution shown as markers

6.0 Budget Period 5

Budget Period 5 (BP5) spanned FY2017 and FY2018, with an emphasis on hydrate dissociation with nitrogen injection and verification of the developed geomechanics capabilities via an international code comparison study. The total PNNL budget for BP1 was \$100,000.

6.1 BP5 Objectives and Scope

A collaborative effort jointly-supported by DOE/NETL and the Korea Institute of Geoscience and Mineral Resources (KIGAM) is planned to be conducted in BP5. During BP4, DOE/NETL provided funding support to verify STOMP-HYDT-KE against swapping experiments previously conducted at KIGAM on hydrate bearing core samples (White et al., 2107). This work demonstrated the ability of the STOMP-HYDT-KE to model the process of exchanging hydrate guest molecules, but additionally demonstrated the limitations of using this approach to economically produce methane hydrates from geologic reservoirs. Recent experimental research (Zhang et al., 2017) has demonstrated the potential of producing methane hydrates by injecting pure nitrogen, yielding unstable thermodynamic conditions for hydrate and dissociation of the hydrate. The objective for KIGAM supported research during BP5 was to investigate the potential for the nitrogen injection technology for methane hydrate reservoirs at the UBGH2-6 Site within the Ulleung Basin of the Korean East Sea. The KIGAM supported research during BP4 was directed at developing geomechanical modeling capabilities within STOMP-HYDT-KE. This work resulted in fundamental porothermoelastic geomechanical modeling capabilities with coupling between the flow and transport and geomechanics components of the code being via a fixed-stress approach. Geomechanics was implemented in the simulator via the finite-element method using the hexahedral based finite-volume grid scheme. Whereas the geomechanical capabilities were demonstrated on a series of benchmark problems with analytical solutions, the testing and code verification has been limited. During BP5 the DOE/NETL funded research continued the verification process for the STOMP-HYDT-KE with its new geomechanics capabilities via independent checks and participation in the second international gas hydrate code comparison study.

For BP5, the joint Korea-US collaborative hydrate project has related, but independent scopes: 1) investigating the potential for nitrogen injection as a methane hydrate production technology for deposits in the Ulleung Basin of the Korean East Sea (KIGAM-funded); 2) verifying the porothermoelastic geomechanical capabilities (DOE/NETL-funded); 3) co-lead the second international hydrate code comparison study (DOE/NETL-funded). The KIGAM funded portion of the project has a single scope topic: assessing the production of natural gas hydrate bearing formations via nitrogen injection. The assessment considered representative natural gas hydrate bearing formations from the Suboceanic Gas Hydrate Deposits at the UBGH2-6 Site within the Ulleung Basin of the Korean East Sea. Numerical simulations were designed and executed that consider the injection of nitrogen into natural gas hydrate bearing formations, whose ambient temperature and pressure conditions are within the stability zone for pure methane hydrates, but outside of those for pure nitrogen hydrates. Multiple well configurations were considered. The DOE/NETL funded portion of the project has two related scope topics: verifying coupled geomechanics and participating in the second international hydrate code comparison study. The overall objective for the DOE/NETL funded activities were the benchmarking and verification of geomechanics in STOMP-HYDT-KE, but this was partially achieved through a new international hydrate code comparison study, that is being led by PNNL (Mark White), LBNL (Tim Kneafsey), and NETL (Yongkoo Seol). Funding supplied was used to jointly support PNNL's leadership of the study, participation in the study, and required modifications to the STOMP-HYDT-KE simulator. We anticipated that the study would be a multiple-year effort, and that during the first year, problems would be developed and solved involving conventional hydrate production without geomechanics and then benchmark-class problems involving coupled hydrate production and geomechanics. One significant difference between geomechanics in other versions of the STOMP simulator and specifically the

STOMP-HYDT-KE simulator was the role of hydrate on the mechanical properties of the formation. In STOMP-CO₂ pore pressure and temperature changes alter the effective stress, but there is not an equivalent hydrate structure to consider. A portion of the funding supplied by DOE/NETL was used to implement these algorithms and mechanistic models into the simulator. Therefore, we envision three thrusts: 1) code comparison study lead, 2) code comparison participation, 3) geomechanics verification, and 4) mechanistic model development and implementation.

PNNL planned to conduct a series of numerical simulations using its STOMP-HYDT-KE simulator with the recently implemented geomechanics solver (GEOMech) to assess the feasibility of the nitrogen injection technology for production of natural gas hydrates from representative formations from the Suboceanic Gas Hydrate Deposits at the UBGH2-6 Site within the Ulleung Basin of the Korean East Sea. Dissociation of natural gas hydrates alters the mechanical properties of the hydrate bearing formation, with the disappearance of the clathrate structure. Dissociation through depressurization additionally increases the mean effective stress (i.e., compressive stress being positive), potentially leading to the subsidence of the overlying layers, including the sea floor. Dissociation through the injection of nitrogen has the potential of maintaining or partially maintaining the mechanical integrity of the hydrate-bearing formation by limiting increases in the mean effective stress. This task involved the development, execution, and evaluation of a series of numerical simulations of nitrogen injection through injector wells and natural gas production through production wells. The simulations considered variations in formation petrophysical properties, initial hydrate saturations, ambient pressure and temperature conditions, well configurations, and operating injection rates and production backpressures. The objective was to seek scenarios under which natural gas could be produced and the mechanical stability of the formation fully or partially maintained. Scientific interest in producing methane hydrates via nitrogen injection has been growing since the work of Haneda et al. (2005). Recent experimental work directed at this technology has included a number of publications and manuscripts (Sakamoto et al., 2007; Masuda et al., 2008; Haneda et al., 2009; Zhang et al., 2017). If the nitrogen injection technology proves feasible, future work could potentially consider the stabilization of a producing formation via injection of carbon dioxide.

PNNL planned to develop algorithms for its STOMP-HYDT-KE simulator for computing the geomechanical properties as a function of hydrate saturation. To complete this task a literature search was conducted to identify an appropriate (i.e., scientifically defensible with reasonable implementation effort) model on which to base the algorithm. In the current version of the simulator mechanical properties for Young modulus and Poisson's ratio are assumed to be spatially variant, but temporally constant. Once implemented the mechanical properties of the rock/soil was to be dependent on hydrate saturation, which would yield temporal variations in geomechanical properties with changes in hydrate saturation. Once fully implemented into the simulator as second literature search would be conducted to identify appropriate problems (i.e., those with hydrate saturation dependent geomechanical properties and known solutions), against which the STOMP-HYDT-KE numerical simulator can be verified. The simulator would then be executed and compared against the known solutions. Differences in results between the simulations and known problem solutions would be evaluated to determine if further code modifications are required.

PNNL would participate in the 2nd International Gas Hydrate Code Comparison Study (IGHCCS-2), entitled "Modeling THM Effects on Gas Production from Hydrate-Bearing Reservoirs," as both participant (i.e., submitting solutions) and co-lead. The other co-leaders for this code comparison study would be Tim Kneafsey from Lawrence Berkeley National Laboratory and Yongkoo Seol from the National Energy Technology Laboratory. The study would be particularly focused on modeling coupled thermal, hydrological, and geomechanical processes and their effect on the production of methane gas from hydrate-bearing reservoirs. This study would build on the accomplishments of 1st International Gas Hydrate Code Comparison Study (IGHCCS-1), successfully executed from 2007 to 2009, and consider the expanded number of numerical simulators worldwide and advances in modeling capabilities of those analytical tools.

The 1st International Gas Hydrate Code Comparison Study (IGHCCS-1) was initially led by Joe Wilder and then later by Brian Anderson and involved the development of a suite of hydrate related problems, teleconferences to discuss problems and solutions, solution submittals by participants, and finally publication of the results. The problems varied in difficulty to those that isolate specific processes associated with the production of methane hydrates from geologic reservoirs to reservoir-scale simulations (Wilder et al., 2008; Anderson et al., 2008; Anderson et al., 2011). Problems were limited to coupled thermal, hydrologic, geochemical processes and considered the production technologies involving depressurization, thermal stimulation, and inhibitor injection. For the 2nd International Gas Hydrate Code Comparison Study (IGHCCS-2), PNNL (Mark White) would co-lead with LBNL (Tim Kneafsey) and NETL (Yongkoo Seol). As with the first study, activities would include the development of problems, conducting teleconferences to discuss problems and their solution, and publishing results. Problems would vary in complexity as before, but additionally included coupled geomechanical processes. An opening workshop was held for the IGHCCS-2 in December 2016, at Lawrence Berkeley National Laboratory. During this workshop initial problems for the study were discussed, and a list of positive attributes and activities for a successful code comparison study was presented by PNNL:

- Collaborative development of problems
- Problem champions
- Start simple
- Identify suite of needed parameters
- Scheduled teleconferences to maintain pace
- International teleconference times
- Impartial host
- Code advancement and verification objective
- Supportive technical discussions
- Dynamic comparison tool
- Selective participation in problem solutions

PNNL would additionally participate in the IGHCCS-2 study as an active participant, bringing its STOMP-HYDT-KE simulator. The new geomechanical modeling capabilities of this simulator would allow solution of problems involving coupled THMC processes. As a participant PNNL would be responsible for developing problem sets, being a problem champion, submitting problem solutions, participating in the study teleconferences, and contributing to the study publications.

6.2 BP5 Accomplishments

During BP5, accomplishments were made against the objectives in three areas: 1) natural gas hydrate production via nitrogen injection, 2) verification of the geomechanics capabilities developed for STOMP, and 3) the second international gas hydrate code comparison study. A synopsis of the accomplishments in each of these three areas is provided in the following sections.

6.2.1 Accomplishments against Modeling Natural Gas Hydrate Production via Nitrogen Injection

A series of numerical simulations were executed on an idealized deposit of marine gas hydrates in the Ulleung Basin, East Sea, Korea. The stratigraphy, initial conditions, petrophysical and transport properties for these simulations were obtained from previous simulation and characterization studies (Kim et al., 2018; Kim et al., 2017). The idealizations included a two-dimensional domain with a planar injection and production wells placed 100 m apart, and the mud layers considered as being impermeable. For scoping studies, these idealizations allow the investigation of the technology without more complicated boundary conditions. The fundamental idea was to inject pure nitrogen gas at pressures below its hydrate stability for the ambient temperatures of the hydrate-bearing layers within the UBGH2-6 site and to produce methane from a well maintained at pressures below in-situ formation pressure, generally slightly below the equilibrium pressures for pure methane hydrates at the ambient temperatures. The driving forces for the simulations were constant pressures in the injection and production wells, and heat transfer from the mud layers into the sand layers. The initial simulations of these scenarios used a Dirichlet boundary for the injection well and an Outflow-Dirichlet boundary for the production well. It was noted, however, that during the simulation the formation pressure near the injection well would increase above the injection pressure, yielding methane production in the injection well. For the simulations reported here, an Inflow-Dirichlet boundary condition was imposed for the injection well. In the field, this would be equivalent to having a check valve on the injection well, not permitting backflow, but otherwise maintaining the specified pressure.

Hydrate production via depressurization and its geomechanical impacts to the seafloor sediments and well stability was investigated by Kim et al. (2018), at bottom-hole pressures over the range from 5 to 14 MPa, for a hydrate bearing formation with pore pressures in range from 23.45 to 23.59 MPa. Recommendations from this work were that bottom-hole pressures should be maintained above 9 MPa to avoid compressive failure of the well assembly. This study addresses hydrate production via nitrogen injection, so injection pressure upper limits are additionally a concern. For this investigation the upper pressure limit was to be bound by the minimum principal stress. Vertical stress gradients were obtained from the characterization work of Kim et al. (2017), however, no information concerning the horizontal stress gradients for the Ulleung Basin were located in published literature.

Principal stress gradients have been published for the Kumano Basin, Nankai trough (Miyakawa et al., 2014), which served as an analog for the Ulleung Basin for this study. At site C0002, with a seafloor depth of 1856 m, the hydrate bearing layers in the Nankai trough are within a normal faulting stress regime (i.e., $\sigma_v > \sigma_H > \sigma_h$ or $\sigma_1 = \sigma_v$, $\sigma_2 = \sigma_H$, $\sigma_3 = \sigma_h$). A plot of the maximum and minimum principal stresses is shown in Figure 5, for the Kumano Basin, Nankai trough at site C0002, along with the pore pressure gradient. A fit to the minimum horizontal stress was generated assuming a weighting factor of 0.39 between the pore pressure and vertical (i.e., maximum) principal stress gradients. If a similar relationship between pore pressure, vertical principal stress and minimum horizontal stress is assumed for the Ulleung Basin at site UBGH2-6, then a minimum horizontal stress gradient can be generated as shown in Figure 6. For injection pressures to remain below the minimum principal stress, within the hydrate bearing layers, a nominal injection pressure limit of 24 MPa was established for this study.

For BP5, twelve simulation cases were considered that differed in the injection and production pressures, with the injection pressure being limited to 24 MPa and the production pressure being limited to 9 MPa. For those cases with the injection pressure below initial formation pressure of around 23.5 MPa, the injection well serves as production well until the pressure drops to near the injection pressure, at which point injection of nitrogen gas commences. In Cases 1 through 9, pure nitrogen gas was injected and in Cases 10 through 12, water saturated with nitrogen was injected. Simulations were based on the stratigraphy developed for the UBGH2-6 site from the simulation work of Kim et al. (2018), which is based on the characterization and model parameter development work of Kim et al. (2017). The intent of

this suite of simulations was to identify scenarios that showed promise for further numerical investigation, using more realistic production configurations, such as five-spot patterns. For these scoping calculations the mud layers of Kim et al. (2018) were ignored and a two-dimensional domain was used. The horizontal distance between the planar wells was set at 100 m. The objective of these scoping simulations was to determine if N₂ injection offered an advantage over depressurization, and whether N₂ could be effective within the pressure constraints of the UBGH2-6 site (24 to 9 MPa). Whereas nitrogen gas was shown in the previous report to be effective at the laboratory scale, this study was focused on the technology under field-scale conditions.

Simulations executed against the experimental work of Zhang et al. (2017), demonstrated the ability of the STOMP-HYDT-KE simulator to model the production of natural gas hydrates with nitrogen injection. Whereas these simulations demonstrated the ability of the technology at the laboratory scale where the initial conditions involved low aqueous saturations, there remained uncertainty about application of the approach at the field-scale, where the system would initially be saturated with aqueous and hydrate phases only. To investigate whether nitrogen injection was a viable production technology at the field scale, simulations were executed on an idealization of the UBGH2-6 site, Ulleung Basin, East Sea of Korea. The simulations used the stratigraphy developed by Kim et al. (2018) in their numerical simulations of natural gas hydrate production via depressurization, and the model parameters characterization work of Kim et al. (2017), but only considered the hydrate bearing sand layers, and simplified the domain to two dimensions with the assumption of planar well surfaces. The objective of these simulations was to scope and compare different injection options. The pressure ranges available for production and injection were based on the geomechanical limitations of compressive failure of the well assembly (Kim et al., 2018), and the minimum principal stress.

The thin nature of the hydrate-bearing sand layers at the UBGH-6 site, coupled with the limitation on pressure ranges, hinder the production of natural gas hydrates. Injection of pure N₂ at the upper pressure limit (i.e., 24 MPa), as shown in Cases 1, 2, and 3, suffered from secondary gas hydrate formation between the injection and production wells. The injected N₂ serves to dissociate hydrate or displace CH₄ from the hydrate near the injection, but the liberated CH₄ then forms secondary hydrate toward the production well, yielding a pressure drop between the two wells at the point of secondary hydrate production, which, in turn, creates more secondary hydrate behind the pressure drop. Whereas petroleum engineering concepts would favor using larger pressure differentials to encourage fluid flow between the injection and production wells, the intermediate (Cases 4, 5, and 6) and lower injection pressure scenarios (Cases 7, 8, and 9), showed greater promise for the N₂ injection technology. The most encouraging aspect of these intermediate and low-pressure scenarios, was the rapid response of N₂ injection to the rate of CH₄ production, following a depressurization stage. This merits additional investigations to optimize the scheduling of depressurization and N₂ injection. One negative aspect to N₂ injection is the amount of N₂ that's required to effect complete production of CH₄. A potential mechanism for offsetting this expense might be the use of a water flood following gas injection, such as that used in enhanced oil production with CO₂ injections and alternating water injections. The water injection scenarios (i.e., Cases 10, 11, and 12) additionally showed promise, but it was unclear as to the contribution of the dissolved N₂ in these simulations.

6.2.2 Accomplishments against Verifying the Geomechanics Modeling Capabilities in STOMP-HYDT-KE

In BP4, the geomechanical module for STOMP, entitled GEOMech, was demonstrated against an analytical solution, of the Terzaghi Poroelastic Deformation problem (Verruijt, 2013). This one-dimensional deformation problem involves the compaction of fluid filled rock under a constant vertical stress. The stress plate is assumed to be highly permeable, allowing pressurized fluid to be expelled. As fluid leaves the system the rock compresses and a new equilibrium state is reached. Whereas, this problem served to demonstrate the core capabilities of the GEOMech module, it was not a problem that

additionally involved gas hydrates. The U.S. DOE NETL collaborative project to this project supports PNNL's roles in the 2nd International Gas Hydrate Code Comparison Study, which is focused on coupled natural gas hydrate production and geomechanics problems. PNNL is serving a lead and participant role in this study. This study has established five benchmark class problems, each with a problem champion. Benchmark Problem 2 is similar in nature to the Terzaghi problem, but was modified by Shubhangi Gupta from GEOMAR, Kiel, to include hydrate dissociation and reformation in response to a time varying imposed stress. The results have not been published, so the solutions from the other participating teams would not be shown, but it should be noted that the PNNL results, generated with STOMP-HYDT-KE show good agreement with the other submissions. A key element to note in the problem is that the composite shear modulus, which makes the shear modulus dependent on the hydrate saturation (i.e., the strength of the hydrate-bearing formation is dependent on the hydrate saturation).

6.2.3 Accomplishments against IGHCCS2 Objectives

The 2nd International Gas Hydrate Code Comparison Study (IGHCCS2) comprises 55 participants, representing 25 teams, from 5 countries (i.e., United States, United Kingdom, Germany, Korea, Japan, and China). The principal communication and code comparison mechanism is teleconferences, which are held on a regular basis. A listing of the teleconference agendas and dates are shown below. The study's inaugural teleconference was held in early November 2017. The study additionally uses the NETL EDX system for distributing information and collecting solution submissions. Teleconferences are recorded and these recordings along with the presentations are stored on the NETL EDX system. The study is currently focused on a series of benchmark problems. Each benchmark problem has a problem champion.

The first benchmark problem is championed by Mark White at PNNL, USA and involves straight hydrate dissociation via either thermal stimulation or depressurization. This problem was part of the 1st International Gas Hydrate Code Comparison Study and does not include a geomechanical component. Eight teams submitted solutions to Benchmark Problem 1; University of Texas, Austin (UTA), Lawrence Berkeley National Laboratory (LBNL), University of California Berkeley (UCB), Pacific Northwest National Laboratory (PNNL), Jilin University (JLU), National Energy Technology Laboratory (NETL), Lawrence Livermore National Laboratory (LLNL), and GEOMAR Kiel (GEOMAR). Those solutions were compared during the IGHCCS2 teleconference series. The second problem is championed by Shubhangi Gupta, GEOMAR Kiel, Germany and is an extension of the classical Terzaghi Problem with four cases. The first case maintains the temperature outside of the hydrate stability zone; the second case yields hydrate formation and dissociation, the third case alters composite mechanical strength of the hydrate bearing layer, and the fourth case considers rapid hydrate formation and dissociation kinetics. Five teams submitted solutions to Benchmark Problem 2: GEOMAR Kiel (GEOMAR), University of California Berkeley (UCB), Pacific Northwest National Laboratory (PNNL), Lawrence Livermore National Laboratory (LLNL), and GEOMAR Kiel (GEOMAR). Submitted solutions were compared during the IGHCCS2 teleconference series. The third benchmark problem is championed by Matt Reagan, Alejandro Queiruga, and George Moridis, at LBNL, USA and considers coupled flow, transport and geomechanics in a radial domain. Eight teams submitted solutions to Benchmark Problem 3; Lawrence Berkeley National Laboratory (LBNL), University of California Berkeley (UCB), Jilin University (JLU), National Energy Technology Laboratory (NETL), and Lawrence Livermore National Laboratory (LLNL). The fourth benchmark problem is championed by Sayuri Kimoto at Kyoto University, Japan and is modeled after the Nankai Trough field experiment. The fifth benchmark problem is championed by Shun Uchida at Rensselaer Polytechnic Institute and considers isotropic consolidation with hydrate dissociation. This problem is particularly interesting as a code comparison study problem, as it requires solution on a single grid cell. To date, no solutions have been submitted against this problem.

- Teleconference #1: November 9, 2017
 - Introductions
 - NETL's Energy Data eXchange (EDX)
 - Code Description Presentation Series
 - Initial Benchmark Problems
 - Hydrate dissociation via depressurization from 1st IGHCCS problem set
 - Terzaghi's poroelastic deformation problem
- Teleconference #2: December 7, 2017
 - T+H Code Description Overview, Matt Reagan (LBNL)
 - STONE Code Description Overview, Alejandro Queiruga (LBNL)
 - T+M and T+F Code Description Overviews, Jihoon Kim (Texas A&M University)
 - HydrateBiot Code Description Overview, Yilong Yuan (Jilin University)
 - Coupled Hydromechanical Benchmark Problem, Mark White (PNNL)
- Teleconference #3: January 11, 2018
 - A THCM Code for Methane Hydrate Reservoirs - Numerical Implementation and Benchmarks, Shubhangi Gupta (GEOMAR Kiel, Germany)
 - CODE_BRIGHT-HYDRATE Code Description Overview, Marcelo Sánchez (Texas A&M University, USA)
 - Coupled Hydromechanical Benchmark Problem, Mark White (PNNL, USA)
- Teleconference #4: January 25, 2018
 - COMVI-MH Code Description Overview, Sayuri Kimoto (Kyoto University, Japan)
 - UC Berkeley THM Code and Constitutive Models Description Overview, Kenichi Soga (UC Berkeley, USA)
 - STOMP-HYDT-KE Code Description Overview, Mark White (PNNL, USA)
- Teleconference #5: February 08, 2018
 - NETL-Pitt Hydrate Simulator Code Description Overview, Jeen-Shang Lin (University of Pittsburgh, USA)
 - K-Hydrate Simulator Code Description Overview, Jung-Tae Kim (KAIST, Korea)
 - Geo-COUS Simulator Code Description Overview, Hosung Shin (University of Ulsan, Korea)

- Teleconference #6: February 22, 2018
 - IGHCCS2 Benchmark Problem #1 Description, Mark White (PNNL, USA)
 - IGHCCS2 Benchmark Problem #2 Description, Shubhangi Gupta (GEOMAR Kiel, Germany)
- Teleconference #7: March 08, 2018
 - IGHCCS2 Benchmark Problem #1 Scheduling and Problem Submission Questions, Mark White (PNNL, USA)
 - IGHCCS2 Benchmark Problem #2 Possible Problem Settings and Scheduling, Shubhangi Gupta (GEOMAR Kiel, Germany)
- Teleconference #8: March 22, 2018
 - IGHCCS2 Benchmark Problem #3 Problem Description and Discussions, Matt Reagan and Alejandro Queiruga (LBNL, USA)
- Teleconference #9: April 12, 2018
 - IGHCCS2 Benchmark Problem 2
 - Review of problem description
 - GEOMAR solutions
 - Discussion on number of simulations
 - IGHCCS2 Benchmark Problem 1
 - Review of problem questions
 - Review of submitted solutions
 - UT Austin, LBNL, UC Berkeley, PNNL
- Teleconference #10: April 26, 2018
 - IGHCCS2 Benchmark Problem 1
 - Review of submitted solutions
 - Discussion of numerical approaches
 - Discussion of difficulties
 - Submitted Solutions
 - University of Texas, Austin (UTA)
 - LBNL, UC Berkeley, PNNL, JLU, NETL

- Teleconference #11: May 10, 2018
 - IGHCCS2 Benchmark Problem 1
 - Review of submitted solutions
 - Discussion of numerical approaches
 - Discussion of difficulties
 - Submitted Solutions
 - University of Texas, Austin (UTA)
 - Lawrence Berkeley National Laboratory (LBNL)
 - University of California Berkeley (UCB)
 - Pacific Northwest National Laboratory (PNNL)
 - Jilin University (JLU)
 - National Energy Technology Laboratory (NETL)

- Teleconference #12: May 31, 2018
 - IGHCCS2 Benchmark Problem 1
 - Update of submitted solutions
 - Submitted Solutions
 - University of Texas, Austin (UTA)
 - Lawrence Berkeley National Laboratory (LBNL)
 - University of California Berkeley (UCB)
 - Pacific Northwest National Laboratory (PNNL)
 - Jilin University (JLU)
 - National Energy Technology Laboratory (NETL)
 - IGHCCS2 Benchmark Problem 2
 - Review of Problem Description
 - Review of Submission Template

- Teleconference #13: June 21, 2018
 - IGHCCS2 Benchmark Problem 1
 - Update of submitted solutions
 - University of Texas, Austin (UTA)
 - Lawrence Berkeley National Laboratory (LBNL)
 - University of California Berkeley (UCB)
 - Pacific Northwest National Laboratory (PNNL)
 - Jilin University (JLU)
 - National Energy Technology Laboratory (NETL)
 - Lawrence Livermore National Laboratory (LLNL)
 - IGHCCS2 Benchmark Problem 2
 - Review of submitted solutions
 - GEOMAR
 - University of California Berkeley (UCB)
 - Pacific Northwest National Laboratory (PNNL)

- Teleconference #14: July 05, 2018
 - IGHCCS2 Benchmark Problem 2
 - Update of submitted solutions
 - GEOMAR
 - University of California Berkeley (UCB)
 - Pacific Northwest National Laboratory (PNNL)
 - Lawrence Berkeley National Laboratory (LBNL)

- Teleconference #15: July 26, 2018
 - IGHCCS2 Benchmark Problem 2
 - Update of submitted solutions
 - GEOMAR
 - University of California Berkeley (UCB)
 - Pacific Northwest National Laboratory (PNNL)
 - Lawrence Berkeley National Laboratory (LBNL)
 - Lawrence Livermore National Laboratory (LLNL)
 - National Energy Technology Laboratory (NETL)
 - IGHCCS2 Benchmark Problem 3
 - Problem description
 - Preliminary solutions
 - Matt Reagan, Alejandro Queiruga, and George Moridis

- Teleconference #16: August 09, 2018
 - IGHCCS2 Benchmark Problem 2
 - Update of submitted solutions
 - GEOMAR
 - University of California Berkeley (UCB) [gas pressure]
 - Pacific Northwest National Laboratory (PNNL)
 - Lawrence Berkeley National Laboratory (LBNL)
 - Lawrence Livermore National Laboratory (LLNL)
 - National Energy Technology Laboratory (NETL) [Case 2 and 3]
 - IGHCCS2 Benchmark Problem 3
 - Problem description
 - Preliminary solutions
 - Matt Reagan, Alejandro Queiruga, and George Moridis

- Teleconference #17: August 09, 2018
 - Potential Benchmark Problem 5
 - Isotropic consolidation test with hydrate dissociation
 - Problem Champion: Shun Uchida (RPI)
 - IGHCCS2 Benchmark Problem 1
 - Update of submitted solutions
 - GEOMAR
 - IGHCCS2 Benchmark Problem 2
 - Update of submitted solutions
 - National Energy Technology Laboratory (NETL) [Case 4]
 - IGHCCS2 Benchmark Problem 3
 - Review of submitted solutions
 - Lawrence Berkeley National Laboratory (LBNL)
 - Lawrence Livermore National Laboratory (LLNL)

- Teleconference #18: September 13, 2018
 - Benchmark Problem 4 (Nankai Trough)
 - Problem description
 - Preliminary solutions
 - Sayuri Kimoto, Kyoto University

- Teleconference #19: September 27, 2018
 - IGHCCS2 Benchmark Problem 3
 - Review of submitted solutions
 - Lawrence Berkeley National Laboratory (LBNL)
 - Lawrence Livermore National Laboratory (LLNL)
 - Jilin University (JLU)
 - National Energy Technology Laboratory (NETL)
 - Open Discussions

- Teleconference #20: October 18, 2018
 - Benchmark Problem 5
 - Isotropic consolidation test with hydrate dissociation
 - Problem Champion: Shun Uchida (RPI)
 - IGHCCS2 Benchmark Problem 3
 - Review of submitted solutions
 - Lawrence Berkeley National Laboratory (LBNL)
 - Lawrence Livermore National Laboratory (LLNL)
 - Jilin University (JLU)
 - National Energy Technology Laboratory (NETL)
 - University of California, Berkeley (UCB)
 - Open Discussions

- Teleconference #21: November 8, 2018
 - Benchmark Problem 4
 - Geomechanical parameter resolution
 - Xiang Sun (U.C. Berkeley)
 - Eugene Myshakin (NETL)

- Teleconference #22: December 6, 2018
 - New Look for the EDX System
 - Revisions and Clarifications on Benchmark Problem 4
 - Problem Description for Benchmark Problem 5
 - AGU Presentation
 - Problem Solution Submissions
 - Benchmark Problem 1
 - University of Ulsan (Ulsan)
 - Benchmark Problem 2
 - University of Ulsan (Ulsan)
 - Jilin University (JLU)
 - Benchmark Problem 4
 - University of Kyoto (Kyoto)
 - University of Ulsan (Ulsan)

- Teleconference #23: December 20, 2018
 - Overview of the Code-Bright-Hyd Simulator
 - Maria de la Fuente Ruiz, National Oceanography Centre, UK
 - Problem Description for Benchmark Problem 5
 - Shun Uchida, Rensselaer Polytechnic Institute, USA
 - Problem Solution Submissions
 - Benchmark Problem 4
 - University of Kyoto (Kyoto)
 - Lawrence Livermore National Laboratory (LLNL)
 - University of California (UCB)

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