Project Title: Kinetic Parameters for the Exchange of Hydrate Formers

Award Number: 65213

Submitting Official: Mark D. White, Research Engineer, PNNL

Project Period: Begin: 07/01/2013 End: open

Reporting Period: Begin: 10/01/2014 End: 12/31/2014

Report Term: Quarterly

Executive Summary

Through the funding support of the U.S. Department of Energy under this Field Work Proposal the Pacific Northwest National Laboratory (PNNL) will investigate numerically and experimentally an unconventional technology for producing geologic accumulations of natural gas hydrates. 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 selected to maintain the original hydrate structure and be thermodynamically preferred under the reservoir temperature and pressure conditions. The numerical component of the proposed work will investigate the Iġnik 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 experimental component of the proposed research will provide 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 proposed work.

Goals and Objectives

This project will investigate the kinetics associated with the production natural gas from hydrate bearing geologic media via unconventional technologies. The principal production technology of concern for this research will be that of exchanging CO_2 and N_2 with clathrated CH_4. The so-called guest-molecule exchange technology is an attractive technology from the perspective of its potential for maintaining the geomechanical integrity of the reservoir formation, in addition to its carbon neutral potential. As with other unconventional technologies its realization to produce natural gas will depend on an understanding of the processes and our ability to exploit this understanding. The approach in this project will be to understand the kinetic mechanisms that control the exchange of hydrate formers using numerical simulation to interpret field-scale trials, laboratory experiments to

determine kinetic parameters, and code comparison to verify mathematical models and solution schemes.

Budget Period 1

During the first budget period, this project will investigate the kinetics of exchanging CO_2 and N_2 with clathrated CH_4 in hydrate bearing geologic media. The project comprises two distinct components: 1) numerical investigation of the 2012 Iġnik 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 will be to provide an interpretation of the data gathered at Iġnik Sikumi Well #1. The experiment component of this project is designed to provide kinetic exchange parameters needed in the numerical simulation. The principal objective of the two experiments is to provide an order of magnitude value to the kinetic exchange parameters for the field-scale simulations of the Iġnik Sikumi gas hydrate field trial.

Budget Period 2

During the second budget period, this project will continue and expand the investigations of the first budget period. Numerical simulations of the 2012 Iġnik Sikumi gas hydrate field trial will continue to resolve disagreements between simulation results and field trial observations, and to provide a more thorough interpretation of the field results. Laboratory experiments designed to provided kinetic parameters under controlled conditions will continue, and a code comparison study will start that will be directed at expanding the International Hydrate Code Comparison Study to problems involving gas hydrates of mixtures of CH_4, CO_2, and N_2 hydrate formers. A suite of problems for the code comparison study are currently being prepared by West Virginia University, which involve hydrates of pure components and component mixtures of CH_4, CO_2, and N_2. The laboratory experiments and code comparison study are currently unfunded.

Technical Highlights, Results and Discussion

This project is divided into budget periods and tasks.

Budget Period 1

Iġnik Sikumi History Match

The paper for the 2014 Offshore Technology Conference, entitled “Guest Molecule Exchange Kinetics for the 2012 Iġnik Sikumi Gas Hydrate Field Trial,” was completed and submitted. Contributions to the paper for the International Conference on Gas Hydrates (ICGH8-2014) to be held in Beijing, China, 28 July – 1 August, 2014, entitled “Review of the findings of the Ignik Sikumi CO_2-CH_4 gas

hydrate exchange field trial," was submitted to Brian Anderson at West Virginia University. Both of these papers document the simulations conducted under this project with the STOMP-HYDT-KE simulator on the Ignik Sikumi #1 Field Trial.

CH_4-CO_2-N_2 Exchange Study

Laboratory efforts during Q1 of FY15 focused on initiating gas hydrate experiments. Staff had previously secured the use of a water chiller, thermocouples and digital meters, gas cylinders of N_2, CH_4, and CO_2, an ISCO high-pressure syringe pump, gas sampling values, and a residual gas analyzer. A previously used HYDEX pressure column, various Swagelok fittings and valves were also located and identified for use under this project. 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 Iġnik 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°C by circulating chilled fluid though the tubing. The column was then pressurized to 1,000 psi with CH_4 and cooled to -2°C, and subsequently cycled between +2° and -2°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°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 value. 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 (~18°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 will repeat this experiment with the addition of a flushing step to remove any free CH_4 in the column prior to disassociating the hydrate.

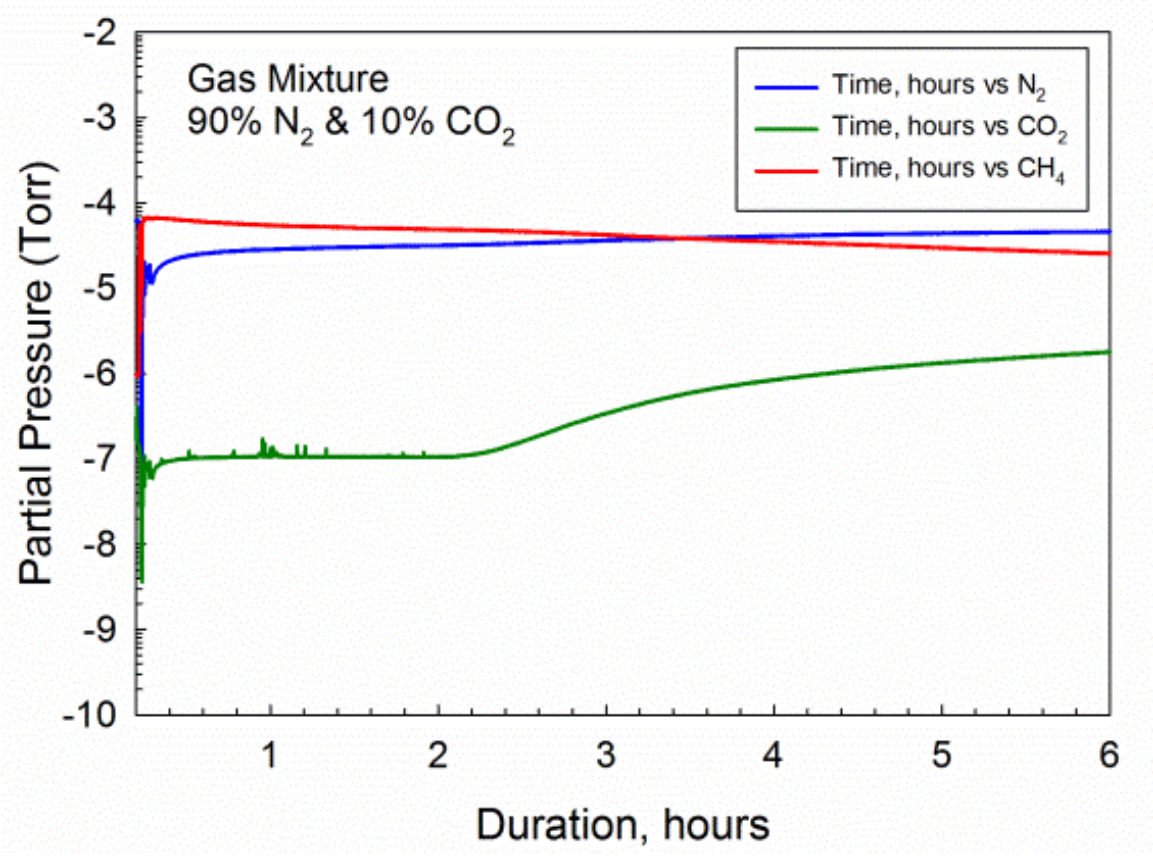

Figure 1. Partial pressure values of CO_2, N_2, and CH_4 obtained from continuous gas sampling of a CH_4 hydrate bearing porous sand column during a titration of 90% N_2 and 10% CO_2 gas mixture (flow at 0.5 ml/min).

Pressurized X-Ray Diffraction Study

There is no progress to report.

Budget Period 2

Iḡnik Sikumi History Match

The Korea Institute of Geoscience and Mineral Resources (KIGAM) funded a numerical simulation study of production technologies at the UBGH2-6 site within the Ulleung Basin of the Korea East Sea. This study is closely aligned with this study in that the STOMP-HYDT-KE simulator was applied to natural gas hydrate production using an injection of a gaseous mixture of N_2 and CO_2 into a natural gas hydrate bearing geologic reservoir. The KIGAM study was conducted during the 1st quarter of FY2015. Whereas, the petrology of the UBGH2-6 hydrate-bearing reservoir differs from that of the Ignik Sikumi #1 Field Trial, the production technology investigated was similar to that used during the Ignik Sikumi #1 Field Trial. Two production scenarios involving the injection of gaseous mixture of N_2 and CO_2 were considered in this study: 1) 40-acre five-spot pattern, and 2) single-well cyclic injection and production. A key finding from the study was that the proper selection of injection and extraction pressures could yield hydrate dissociation and mechanical stability to the formation. During the 2nd quarter of FY2015 these numerical investigations will be continued to assess the potential for long-term performance and commercial-scale production rates. The numerical simulation studies of the Ignik Sikumi #1 Field Trial, will additionally start during the 2nd quarter of FY2015 and will also include assessments of long-term performance and commercial-scale production rates, based on the findings of the KIGAM supported study.

Code Comparison Study (Currently Unfunded)

This task is currently unfunded.

CH_4-CO_2-N_2 Exchange Study (Currently Unfunded)

This task is currently unfunded.

Pressurized X-Ray Diffraction Study (Currently Unfunded)

This task is currently unfunded.

Risk Analysis

The risks associated with this project are those described in the Project Management Plan.

Schedule/Milestone Status

Budget Period 1

Iġnik Sikumi History Match

Title: Review Archived Data

This milestone was completed in preparing for the numerical simulations of the Ignik Sikumi #1 Field Trial. This work is documented in the OTC 2014 paper (White and Lee, 2014).

Title: Simulate Ignik Sikumi Field Trial

This milestone was completed in conducting the numerical simulations of the Ignik Sikumi #1 Field Trial. This work is documented in the OTC 2014 paper (White and Lee, 2014).

Title: Compare Simulation Results

This milestone was completed in writing the contribution to the ICGH8-2014 paper with Brian Anderson (Anderson et al., 2014).

Title: Report Interpretations

This milestone was completed by writing two papers documenting the comparison of the STOMP-HYDT-KE simulations against the field observations from the Ignik Sikumi #1 Field Trial (White and Lee, 2014; Anderson et al., 2014).

Budget Period 2

Title: Submit a Manuscript to a Peer-Reviewed Journal

This milestone is uncompleted.

Cost Status

This quarter concluded with a cost variance of about $49.7k, due to the delayed start of the pressurized x-ray diffraction study and the numerical Ignik Sikumi study. The cost status spreadsheet is shown on the following page.

Conclusion

KIGAM continued to support gas hydrate production investigations this fiscal year at PNNL in the spirit of the joint Korea-U.S. gas hydrate research project, under the leadership of Dr. Won Suk Lee. The result of this support was the application of STOMP-HYDT-KE to the numerical investigation of three production technologies

for natural gas hydrates at the UBGH2-6 Site within the Ulleung Basin of the Korea East Sea. The three production technologies included single-well depressurization, single-well cyclic flue gas injection, and 42-acre five spot flue-gas injection and production. A report of the simulations and findings were provided to KIGAM. The first trial of the CH_4-CO_2-N_2 exchange study experiment was successfully completed. A second trial at 2˚C and 750 psi is planned. The second trial conditions will put the injected gas out of hydrate stability conditions and the in-situ methane within hydrate stability conditions, similar to those conditions investigated numerically for production technologies at the UBGH2-6 Site, supported by KIGAM.

References

White, M.D. and W.S. Lee. 2014. "Guest molecule exchange kinetics for the 2012 Ignik Sikumi Gas Hydrate Field Trial," *Proceedings of the Offshore Technology Conference held in Houston, Texas, USA, 5-8 May 2014, OTC-25374-MS*.

Anderson, B., R. Boswell, T. S. Collett, H. Farrell, S. Ohtsuka, and M. White. 2014. "Review of the findings of the Ignik Sikumi CO_2-CH_4 gas hydrate exchange field trial," *Proceedings of the 8th International Conference on Gas Hydrates (ICGH8-2014), Beijing, China, 28 July - 1 August, 2014*.

Baseline Reporting Quarter		FY2013	FY2014				FY2015			
		Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Baseline Cost Plan										
Federal Share	Task 1.0	$1,250	$1,250	$1,250	$1,250	$0	$0	$0	$0	
	Task 2.0	$11,250	$11,250	$11,250	$11,250	$0	$0	$0	$0	
	Task 3.0	$10,000	$10,000	$0	$0	$0	$0	$0	$0	
	Task 4.0	$10,000	$10,000	$0	$0	$0	$0	$0	$0	
	Task 5.0	$0	$0	$0	$0	$0	$1,250	$1,250	$2,500	
	Task 6.0	$0	$0	$0	$0	$0	$25,000	$25,000	$25,000	
Non-Federal Share		$0	$0	$0	$0	$0	$0	$0	$0	
Total Planned Cost (Federal and Non-Federal)		$32,500	$32,500	$12,500	$12,500	$0	$26,250	$26,250	$27,500	
Cumulative Planned Cost		$32,500	$65,000	$77,500	$90,000	$90,000	$116,250	$142,500	$170,000	
Actual Incurred Costs										
Federal Share	Task 1.0	$0	$0	$0	$0	($345)	$84			
	Task 2.0	$0	$21,876	$19,014	$10,139	$0	$0			
	Task 3.0	$0	$418	$2,507	$0	($20)	$12,865			
	Task 4.0	$0	$0	$0	$0	$0	$0			
	Task 5.0	$0	$0	$0	$0	$0	$0			
	Task 6.0	$0	$0	$0	$0	$0	$0			
Non-Federal Share		$0	$0	$0	$0	$0	$0			
Total Actual Cost (Federal and Non-Federal)		$0	$22,294	$21,521	$10,139	($365)	$12,949			
Cumulative Actual Cost		$0	$22,294	$43,815	$53,954	$53,589	$66,538			
Variance										
Federal Share	Task 1.0	$1,250	$1,250	$1,250	$1,250	$345	($84)			
	Task 2.0	$11,250	($10,626)	($7,764)	$1,111	$0	$0			
	Task 3.0	$1,250	$832	($1,257)	$1,250	$20	($12,865)			
	Task 4.0	$11,250	$11,250	$11,250	$11,250	$0	$0			
	Task 5.0	$0	$0	$0	$0	$0	$0			
	Task 6.0	$0	$0	$0	$0	$0	$0			
Non-Federal Share		$0	$0	$0	$0	$0	$0			
Total Cost Variance (Federal and Non-Federal)		$32,500	$10,206	($9,021)	$2,361	$365	$13,301			
Cumulative Cost Variance		$32,500	$42,706	$33,685	$36,046	$36,411	$49,712			

Task	Milestone Description	FY13	FY2014				FY2015				Planned Start Date	Planned End Date	Actual Start Date	Actual End Date
		Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4				
Task 2	Review archived data										7/1/13	9/30/13	10/28/13	11/30/13
Task 2	Simulate Ignik Sikumi field trial										10/1/13	12/31/13	12/1/13	3/31/14
Task 2	Compare simulation results										1/1/14	3/31/14	1/1/14	4/8/14
Task 2	Report interpretations										4/1/14	6/30/14	4/1/14	6/30/14
Task 3	Conduct Kinetic Exchange Exp.										10/1/13	12/31/13	1/1/14	
Task 4	Conduct Hydrate Structure Exp.										10/1/13	12/31/13	1/1/14	
Task 6	Publish Manuscript										10/1/14	6/30/15	10/1/14	