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: 10/01/2013 End: 12/31/2013

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 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 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 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 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 will be to provide an interpretation of the data gathered at Ignik 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 Ignik Sikumi gas hydrate field trial.

Technical Highlights, Results and Discussion

This project comprises three distinct tasks; one numerical simulation and two experimental.

Iġnik Sikumi History Match

Numerical simulations to model the Ignik Sikumi #1 field trial were started during the quarter. This work was focused on the injection period of the field trial and comprised developing geologic models, executing the STOMP-HYDT-KE simulator and comparing the results against the data collected during the field trial, as reported in the final report (Schoderbek et al., 2013). Four different geologic models were developed: 1) 1-dimensional radial, 2) 3-tier 2-dimensional radial, 3) isotropic 25-tier 2-dimensional radial, 4) anisotropic 25-tier 2-dimensional radial. All three simulations considered a 306-hr injection period; where, gas was injected at a constant pressure of 1430.4 psi over the screened interval in a molar ratio of $77.5/22.5 N_2/CO_2$.

The 1-dimensional radial domain used average properties of the reservoir and only considered a vertical range that matched the perforated interval of the injection well. The 1-dimensional simulation yielded good agreement with the field trial observations 167.3 Mscf (167.3 x 10^3 scf) of N₂ and 48.6 Mscf (48.6 x 10^3 scf) of CO₂ injected, but the injectionrate profile did not show good agreement. The 3-tier 2-dimensional radial domain used averaged properties over the intervals below, within, and above the perforated interval of the injection well. These simulations yielded injection rate profiles that increased with time as the injected gas migrated into the layers above and below the perforated region, which initially had lower hydrate saturations. The 25-tier 2-dimensional domains used a uniform vertical grid spacing of 2 ft, with different values for porosity, initial hydrate saturation, and intrinsic permeability for each strata. When a vertical to horizontal anisotropy ratio in intrinsic permeability of 0.1 to 1.0 was used, with the intrinsic permeabilities scaled by a factor of 1.5, the numerical simulations showed good agreement with field trial data. These later simulations formed the basis of the manuscript that was submitted to the 2014 Offshore Technology Conference, entitled "Guest Molecule Exchange Kinetics for the 2012 Ignik Sikumi Gas Hydrate Field Trial."

The early deadline for submission of manuscripts to the 2014 OTC required the paper to be submitted before the simulations for the soak and production periods could be completed. These simulations will be completed prior to presentation of the Ignik Sikumi #1 field trial numerical results at the conference. As an example of the simulation results, the state of the hydrate and gas saturations at the end of the injection period (i.e., after 306 hr) is shown in Figures 1 and 2, 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 period both primary hydrate dissociation and secondary hydrate formation occurred. The gas saturation profile is nonuniform 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.



Figure 1. Hydrate saturation at the end of the 306-hr injection period.



Figure 2. Gas saturation at the end of the 306-hr injection period.

CH₄-CO₂-N₂ Exchange and Pressurized X-Ray Diffraction Studies

During this quarter, PNNL completed the remodeling of new laboratory space in the Life Sciences Laboratory (LSL2). Our laboratories in Sigma V were closed, packed, and moved to the new facility. Key instruments were decommissioned, reinstalled in LSL2, and brought back on-line in November. Project staff participated in the move activities and were busy setting up the new lab space during this quarter. Specifically, the vendor supporting the Bruker-AXS XRD unit installed the low temperature stage and associated LN2 tubing onto the computer controlled XYZ low temperature stage. It was tested down to -10C and where it was maintained temperature, within +/- 1C for 5 hours. Additionally, in preparation of the mixed gas exchange experiments, small sample inserts were machined and fitted into the high pressure beryllium XRD reactors. Other required items such as low temperature o-rings, research grade purity gases (N2, CO2, and CH4) were procured and delivered to the new laboratories.

Risk Analysis

The STOMP-HYDT-KE simulator is executing better with respect to convergence stability than its predecessors STOMP-HYD-KE and STOMP-HYD. The STOMP-HYD simulator is an equilibrium-based code, solving five unknowns per grid cell. The STOMP-HYDT-KE is a kinetic-based code, solving nine unknowns per grid cell. Before developing and applying the simulator there was some concern that the additional complexity of the STOMP-HYDT-KE could result in convergence problems. In working with the simulator on the Ignik Sikumi #1 field trial simulations, it currently appears that the opposite is the case. Until the experimental tasks formally begin, the risks associated with the experimental tasks remain those documented in the project management plan.

Schedule/Milestone Status

Iģnik Sikumi History Match

Title: Review archived data and previous simulation attempts. Planned Date: 9/30/2013 Revised Date: 12/31/2013

Numerical simulations to model the Ignik Sikumi #1 field trial for the injection period have been partially completed. The deadline of January 13, 2014 for submitting a manuscript to the OTC 2014 conference has caused a delay in completing the simulations for the soak and production periods of the field trial. With the paper submission complete, simulations will resume.

Cost Status

This quarter concluded with a cost variance of about \$33K, mostly due to project staff being occupied with other project work. It should be noted that there a considerable portion of the funds spent on the numerical simulation tasks were due to the preparation of a

manuscript for the OTC 2014 conference. The cost status spreadsheet is shown on the following page.

Conclusion

The numerical simulation tasks of this project have started and are generating results that show agreement with the Ignik Sikumi #1 field trial. Simulations for the soak and production periods are scheduled to be completed during next quarter. The experimental tasks are scheduled to start next quarter.

References

Schoderbek, D., H. Farrell, K. Hester, J. Howard, K. Raterman, S. Sipngarmlert, K.L. Martin, B. Smith, and P. Klein. 2013. "Oil & Natural Gas Technology: ConocoPhillips Gas Hydrate Production Test: Final Technical Report." United States Department of Energy, National Energy Technology Laboratory, DE-NT0006553-Final-Technical-Report.

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