Oil & Natural Gas Technology

DOE Award No.: DE-NT0006558

Quarterly Report
July 1 – September 30, 2011

Integrating Natural Gas Hydrates in the Global Carbon Cycle

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Prepared for:
United States Department of Energy
National Energy Technology Laboratory

November 10, 2011

Office of Fossil Energy

Progress Report
Agency: DOE NETL
Project title: Integrating Natural Gas Hydrates in the Global Carbon Cycle
Agency Award Number: DE-NT0006558
Report Period 7/1/11 to 9/30/11

Executive Summary

Production runs are underway, I feel certain this time, for the Atlantic margin, Gulf of Mexico, and Arctic simulations. The past months have been a period of adding "one more thing", trying to match observations of the structure of the sediment lens and the chemical reactions that take place within it. We've changed the sediment deposition / resuspension / redeposition physics, added petroleum as a carbon pool interacting with methane, and added deep-sediment weathering reactions to account for observed dissolved CO_2 concentrations. The archetype scenarios have been developed, and have had a synergistic impact on each other, as we try to find a common code that can simulate all of them. The accretionary wedge scenario has been run to equilibrium but it fails to produce sufficient methane. We feel that the solution may lie in the balance between coastal and hemipelagic sedimentation in the simulation, a re-tuning job which should either work or not work relatively quickly.

Approach

1. The passive margin simulations were tuned in their sediment deposition and dispersion rates to match reconstructed envelope of the sedimentary deposits over the crust. Sediment redeposition depending on sea floor slope, a process developed for the accretionary wedge simulation, was added to the mix of sediment transport and deposition mechanics. Also, an imposed crustal subsidence rate was added to the code, which was necessary to achieve the extreme depths of the sediment column, especially in the Gulf simulation. The goal was to simulate more quantitatively the slope of the sea floor on the continental slope, and the depths and onshore / offshore extents of the sediment lenses.

2. The carbon and methane cycles in the code have been revamped and tuned, including changes to the respiration kinetics of POC (the Wallmann effect), and generation of petroleum in the appropriate temperature and H/C environments, with some upward migration and subsequent respiration if temperatures drop below about 50° C (compared with the 60° C lower bound for petroleum generation). The goal is to match the del 13 C of the dissolved inorganic carbon, which rises to +10 per mil in deep pore waters. The model tends to over-predict the del 13 C of the DIC, reaching +20 per mil. The POC respiration rate kinetics are from measurements, but if they were dialed down to limit the DIC del 13 C to +10 per mil, the model wouldn't produce enough methane to make hydrates. I think this is probably coupled to the very mysterious pore water profiles of SO4 and CH_4, which seem to demand a depth-zone with a dearth of methaneogenesis, as evidenced by linear SO4 and CH_4 profiles, capping a zone of much faster methanogenesis below it, as if the kinetics were extremely strongly temperature sensitive.

These are not simple problems, will require higher model resolution and future thought to really get it right.

3. Targeting del 13 C of the DIC necessitated dealing with uptake of CO_2 by deep subsurface reactions with rocks; weathering reactions. Pore-water DIC decreases with depth below the respiration zone, indicating uptake of CO_2 by leaching Ca from igneous rocks, and deposition of $CaCO_3$. The code calculates the equilibrium CO_2 dissolved concentration at the local temperature and assuming the presence of anorthite, a calcium-containing feldspar, and kaolinite, which has lost the calcium, plus calcite. Equilibrium CO_2 is quite low except in the very deepest hottest sediments. The kinetics of the reaction, the approach to equilibrium, are temperature-dependent, allowing DIC to build up in the respiration zone but depleting it in warmer temperatures below. We have tested a version of the code that tracks the entire carbonate buffer system, adding alkalinity and calcium concentrations to the tracked tracers. There was a huge impact of sulfate reduction altering the balance between alkalinity and calcium in the pore waters, leaving long-term effects. Ultimately I concluded that in reality other chemical buffering reactions come into play, and that resolving the chemistry in this detail is not really necessary at this stage anyway. DIC is now taken as a surrogate for dissolved CO_2 concentration. The near equality of DIC and alkalinity concentrations of deep porewater suggests that the pH, and hence the fraction of DIC that is CO_2, doesn't change wildly through the sediment column.

Future Work

1. As long as no one shouts "stop the press", pointing to some new model improvement, the production (non-accelerated) runs are going for the passive scenarios. They take a few weeks to finish, and when they do we can use the end results as restart files to run glacial / interglacial cycles and global warming scenarios, which will not take much computational time. The paper describing the bulk of the model development is relatively polished, but needs figures from the production run, and addition of the new stuff described above. A paper describing the Arctic scenario is also in draft stage, as is one for the active margin (with its additional model description). The Gulf scenario will also be a separate paper, but we need to calculate where in the sediment column salt domes should appear, a function of the density (porosity) of the sediment at the foot of the column and where the salt is found (limited to the transitional crust between continental and ocean crust).

2. The active margin results are surprising because it's not obvious from the model where all the observed methane comes from. The deep sediment column could be a source of thermogenic methane, but there are two objections to this possibility. First, the sediment only gets that deep where the sea floor is fairly shallow, eliminating the hydrate stability zone. Second, the isotopic composition of methane on the Juan de Fuca margin indicates biogenic origins, not thermogenic. So the methane must be coming from POC. The problem is that the sediment moves through the wedge complex fairly quickly, so there is limited time for accumulation of hydrate. The answer may come in adjustment of the pathways of sedimentation. There is primary continental sediment which is dispersed from the left-hand boundary of the simulation, depositing according to water depth and the sinking velocities of the various grain sizes. There is also a "pelagic"

fraction, which deposits laterally uniformly throughout the domain, if the water depth is deep enough. The POC fraction of all of this material is specified as a function of water depth at time of deposition.

If the slope of the sea floor exceeds a critical value (typically 4% is a good fit), erosion resuspends surface sediment for redeposition offshore. The redeposition scheme parallels the primary sediment deposition scheme, with various size fractions depositing according to water depth and their sinking velocity. The POC is conserved in this process, fractionated according to the surface areas of the various size fraction (i.e. enriched with the fines).

In the various passive margin simulations, the best fit for the thickness of the sediment envelope required a relatively high rate of "pelagic" sedimentation, 15 cm/kyr, a rate more typical of relatively near-shore hemipelagic settings, i.e. including turbidites. For the active margin simulation, the pelagic sedimentation rate needs to be high in order to generate a crust 1-2 km thick in the amount of time it took for the crust to arrive from the spreading center.

Our thought is to modify the sediment redeposition to look more like a turbidite than like uniform deposition of a dilute sediment suspension as it is now. Then I'd plan to decrease the "pelagic" deposition to true pelagic values (1 cm/kyr) and adjust the "coastal" sediment influx to recreate the thickness of the incoming sediment column by means of resuspended organic-rich coastal material, rather than "pelagic" material that had a low POC because its initial deposition was in relatively deep water.

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