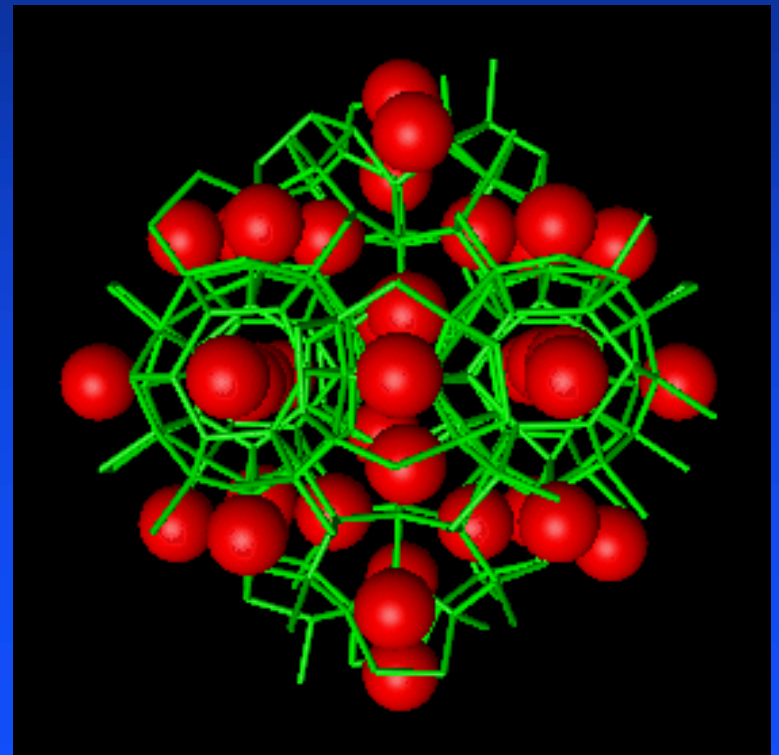


Anti-Agglomerant Low Dosage Hydrate Inhibitors (LDHI's)

Lynn M. Frostman, PhD
Baker Petrolite



Courtesy of Cornell University

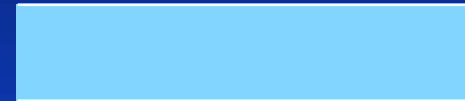
Types of Hydrate Inhibitors

No Inhibitor



**hydrates, possible
plug**

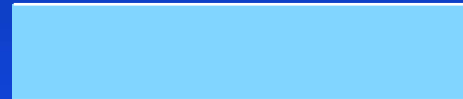
**MeOH, Ethylene
Glycol**



no hydrates

Kinetic Inhibitor

short times



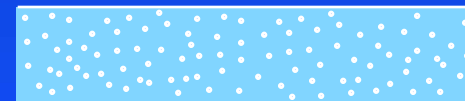
no hydrates

long times



**hydrates, possible
plug**

Anti-Agglomerant



dispersed hydrates

Baker Petrolite's Anti-Agglomerant Inhibitors

● General Characteristics

- Allow hydrates to form
- Hydrate particles remain small, well-dispersed, non-adherent
- Fluid viscosity remains low
- Require liquid hydrocarbon phase (condensate or oil)
- Inject continuously before fluid enters hydrate region
- No known limitation on severity of subcooling
- Effective even after prolonged (2 Week) shut-ins

Anti-Agglomerants

● Primary Advantages

➤ Low Dosage

- Lower Capital Costs
- Lower Chemical Costs
- Lower Transportation Costs
- Lower Storage Costs
- Smaller Pumps
- Less Maintenance

➤ Effective at Severe Conditions

➤ Effective During Extended Shut-ins

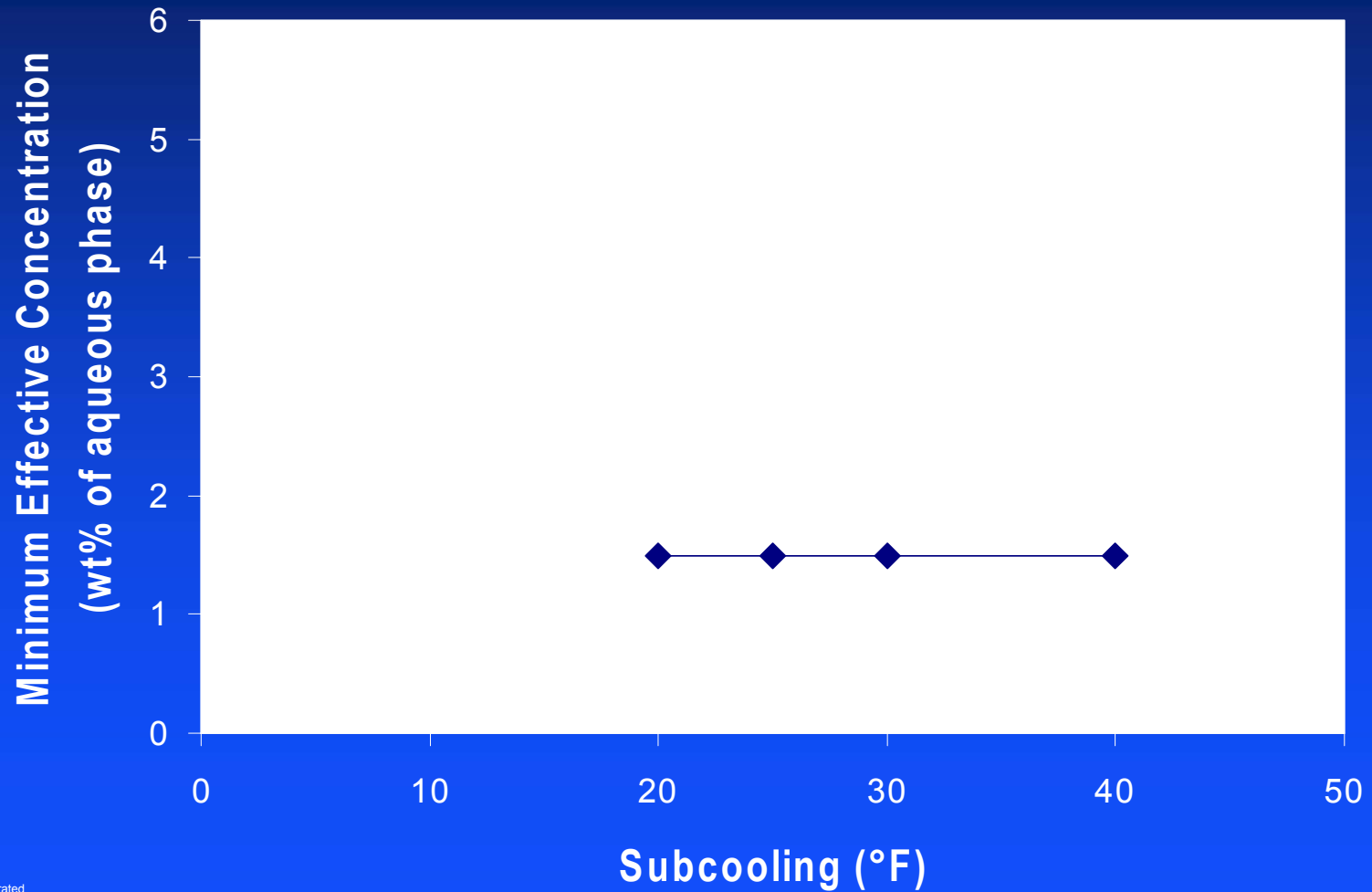
➤ Total System Approach to Ensure Products are Compatible with Production System

Anti-Agglomerants

- **Limitations:**

- **Require liquid hydrocarbon phase and water cut < 50-75%**
- **Do not protect gas phase**
- **May not be effective at temperatures below 38 °F**

Dosage is Independent of Subcooling



Potential CapEx and OpEx Reductions

Currently available LDHI's can:

- Cut treatment cost (\$/bbl water) 50%
- Reduce umbilical diameters 35%
- Reduce number of umbilicals by combination with other production chemicals
- Reduce storage or increase time to resupply 2 orders of magnitude
- Reduce weight of stored chemicals 2 orders of magnitude

Previous and Existing Applications

● Previous

- Deepwater Gulf of Mexico: 1.5 month subsea trial, continuous injection
- North Sea: several brief trials, continuous subsea injection
- New Zealand: 1 brief trial, continuous subsea injection

● Existing

- Deepwater Gulf of Mexico: 2 platforms' dry tree wells, intermittent use only
- Canada: 2 continuous injection, onshore applications

Planned Applications

- **Early June**

- continuous subsea injection in gas condensate line, ~500 gpd

- **July**

- 2 new platforms' dry tree wells, intermittent use only

- **Others**

- 2 week field trial, continuous subsea injection
- brief field trial, continuous topsides injection

Applications Under Consideration

- **Deepwater Gulf of Mexico**
 - 3 platforms' dry tree wells, intermittent use
 - 2 subsea, intermittent use
 - 6 subsea, continuous applications
- **North Sea**
 - 4 subsea, continuous applications
- **Canada**
 - 2 subsea, continuous applications

Potential Concerns with LDHI's

- Impact on desalter
- Impact on biotreater
- Corrosion in the overheads
- Ultimate fate of decomposition products
- Impact on jet fuel and diesel

Potential Concerns with LDHI's

- **Biggest unknown is the expected concentration due to dilution from other production**
- **Typical use concentration: 15,000 ppm basis water**
- **Water cut 1-50%**
- **Intermittent or continuous use**
- **Partitioning strongly depends on nature of oil, salinity of water, and water cut**
 - **high salinity, black oil systems: >95% tends to partition to oil**
 - **low salinity, condensate systems: ~50% tends to partition to oil**

Example: Upcoming Application

- Well making 1000 bwpd, 45 mmscfd
- Pumping 175 bpd MeOH - insufficient to control hydrates
- Have well curtailed to 35 mmscfd
- Plan to pump 500 gpd LDHI
- Should be able to bring back to full production
- Expected LDHI concentration at refinery = 40-50 ppm

Impact on Desalter

- No adverse effects are expected on emulsion tendencies in desalters.
- Experimental test:
 - shake oil and synthetic brine (20% water cut, 16 wt% salinity) with and without LDHI
 - separate oil and water by gravity
 - expect the majority of active ingredient to partition to oil phase (however, we did not specifically measure the partitioning in this sample)
 - EDDA demulsification/dehydration test at 208 °F and 5% water cut
 - LDHI did not adversely affect ability to resolve emulsion
 - LDHI may have in fact helped break emulsion

Impact on Biotreater

- **Partitioning to desalter wash water**
 - under investigation; preliminary data suggests <10% of LDHI in oil will partition to water
- **Toxicity towards biotreater bugs**
 - used an actual sample of bugs from a refinery
 - exposed to different concentrations of RE 4136
 - 100 ppm RE 4136: there was no observed effect compared to a blank
 - at 1000 ppm RE 4136, we observed a significant drop in the bug population.

Overhead Corrosion

- **May be a possibility**
- **Should be treatable**

Ultimate Fate / Impact on Products

- LDHI is expected to decompose in crude distillation unit
- decomposition products have boiling point range overlapping with jet fuel and diesel (390-707 °F)
- impact on jet fuel and diesel under investigation

Plan Forward

- Further partitioning studies under desalter conditions
- Bench scale distillation
 - with and without LDHI's
 - analyze jet fuel and diesel cuts for standard specs
 - jet fuel 350-550 °F
 - diesel 550-700 °F
 - distillate specs as identified by David Bailey
 - crude oil obtained from Equilon
- Pilot scale refinery test?
- Other suggestions?