Effect of Gas Composition on Hydrate Growth Rate and Agglomeration Tendency

Lyon – 13 au 16 juin 2022

Effect of Gas Composition on Hydrate Growth Rate & Agglomeration Tendency

Ross Anderson[1,2*], Morteza Aminnaji[1], Bahman Tohidi[1,2]
[1]*Institute of Geoenergy Engineering, Heriot-Watt University, Edinburgh, EH14 4AS, Scotland, U.K.*
[2]*Hydrafact Ltd., Heriot-Watt University Research Park, Edinburgh, EH14 4AP, Scotland, U.K.*
**email: ross.anderson@hw.ac.uk*

Introduction

Historically, AA studies have focused on:

- Liquid hydrocarbon (L_{hc}) & aqueous phases
- Oil composition / natural surfactants
- Water cut & salinity

Less attention paid to gas & hydrate phase compositions:

- Hydrate = single structure of fixed composition…
- 's-II natural gas hydrates' with 6:1 hydration
- Hydrate % main factor in plugging

But recent JIP studies show that:

- Gas / hydrate composition plays major role in transportability
- Controls hydrate growth rate & plugging tendency
- LDHI performance, including AAs & KHIs

S-II Formation in Simple Methane Systems

At moderate P&T, C_1 is assumed to form s-I. However, rare studies [1,2] have shown it can form s-II (30-90 bar / 1.5–12 °C), albeit this is metastable?

Our studies up to 185 bar show consistent evidence for 2 hydrate structures, assumed as s-I & s-II. Transitions between these are associated with agglomeration.

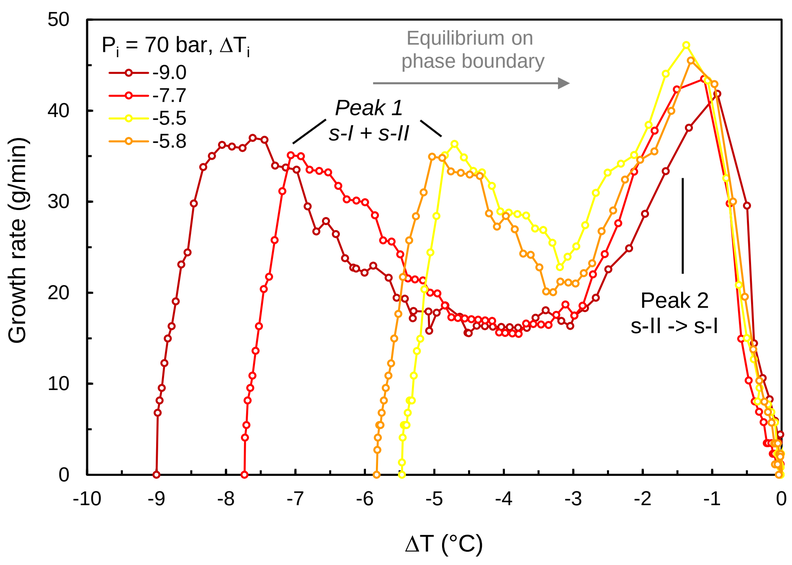


Figure 1. CH_4 hydrate growth rates show two peaks

Initial rapid s-I/s-II formation
⇓
exothermic s-I to s-II (slows) with agglomeration
⇓
Final s-I

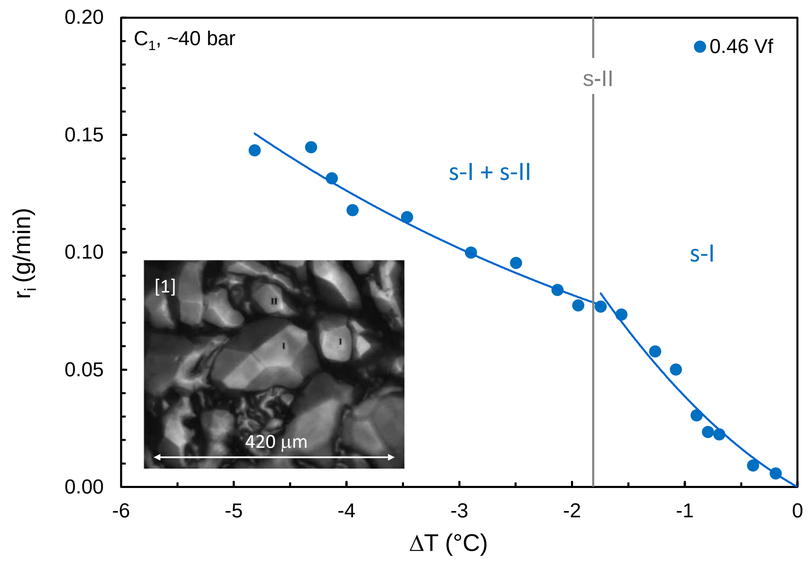


Figure 2. Initial hydrate growth rates (r_i) vs ΔT show a clear change in slope where s-II is predicted

Exothermic s-II → s-I slows growth?

[1] The Coexistence of Two Different Methane Hydrate…
Schicks & Ripmeester (2004) *Angewandte Chemie*, 43, 3310

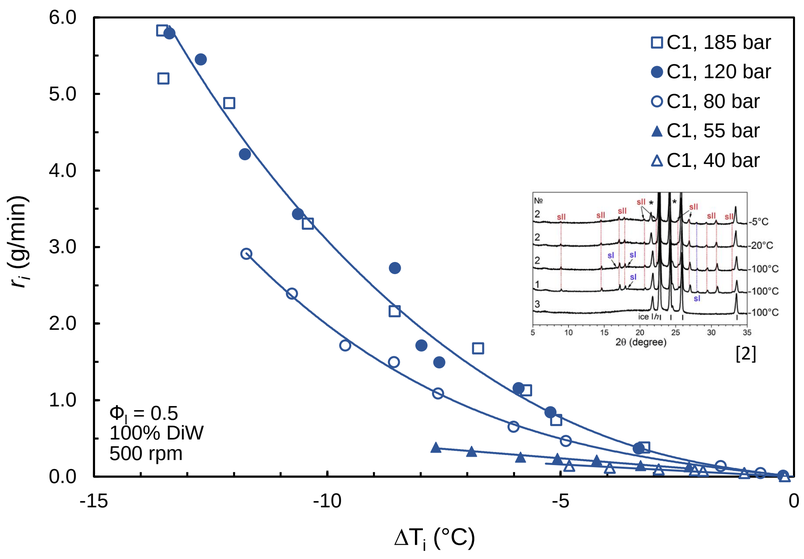


Figure 3. Growth rate data shows unexpected P effect to ~120 bar

ΔT not the only driving force

Variable (re)formation of s-I vs s-II?

[2] Unexpected formation of sII methane hydrate in some water-in-oil emulsions…"
Stoporev et al. (2018), *J. Nat. Gas Sci. Eng.*, 60, 284.

Effect of Gas Composition on Growth Rates & Plugging

In addition to s-I + s-II in single component C_1, multiple structure formation/reformation has been found for multicomponent gases (companion paper [3]).

Different gases show variable plugging tendencies vs ΔT for identical conditions; it is proposed that this is structure change related, e.g. through melting/regrowth cementation.

Rapid growth rates for some purer component phases means initial hydrates may not be most thermodynamically stable, causing subsequent solid-solid and/or complete dissociation-reformation…

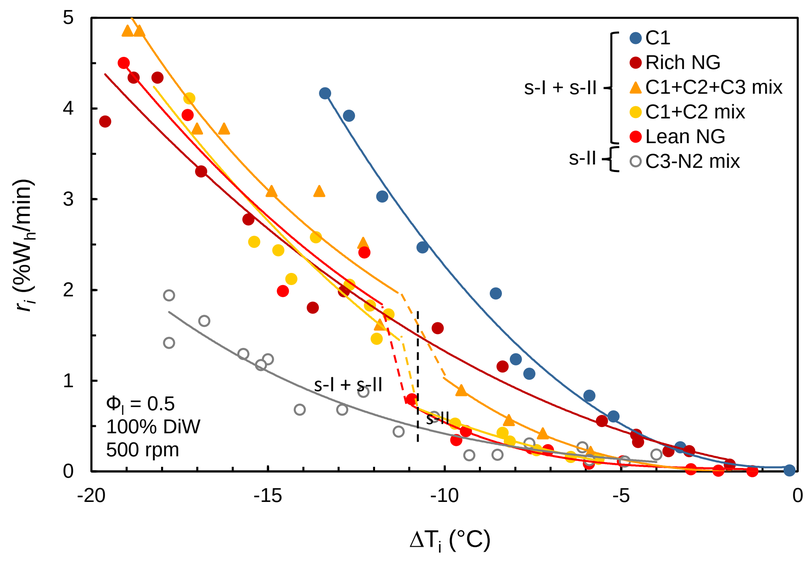


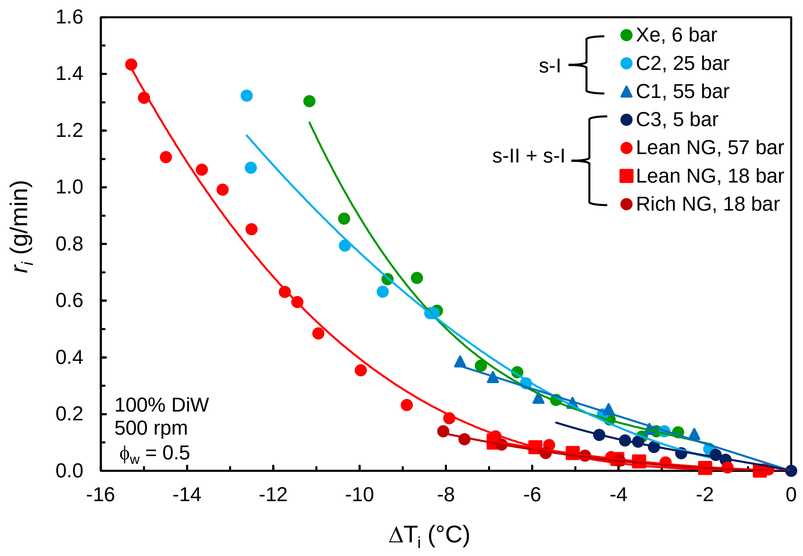
Figure 4. Gas composition has major effect on hydrate growth rates (r_i, % water converted per minute)

s-I more rapid than s-II?

In NGs, s-II at low ΔT, s-I + s-II at high

Figure 5. It is *pure component hydrates* which grow faster than complex, multi-component structures

Pure gas = unlimited local supply of guest gas molecule at growth sites?



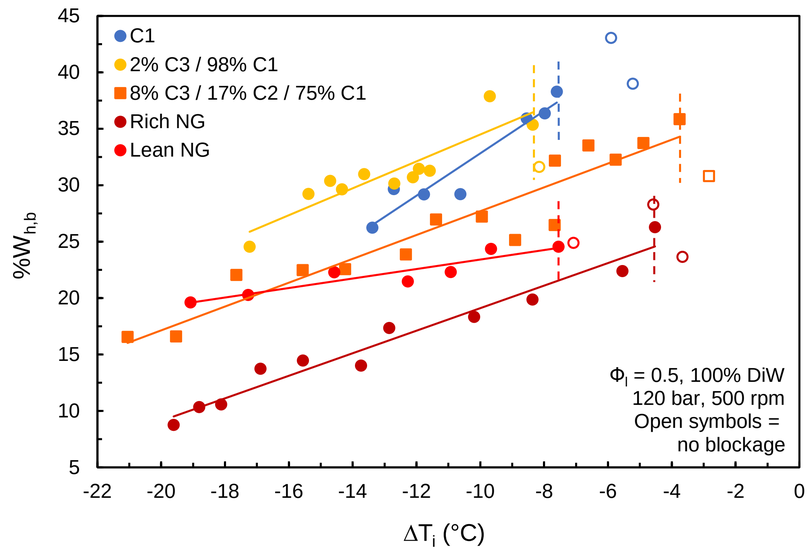


Figure 6. Gas composition has major effect on plugging onset ΔT and hydrate fraction (% water as hydrate which causes blocking)

Richer, multi-component gases show greatest plugging propensity

Conclusions

Gas composition has major effect on growth rates & plugging

- Pure component hydrates grow the most rapidly
- In mixed gases, more pure component (e.g. C_1 s-I/s-II) rich metastable phases form at higher ΔT
- Then reformation (both exo- & endothermic) melting/re-growth occurs
- Leads to grain contact cementation = higher plugging propensity?