
Hochschule Niederrhein
University of Applied Sciences
ILOC
Institut für Lacke und Oberflächenchemie
Institute for Coatings and Surface Chemistry

„Research on inhibition of gas hydrate formation in pipelines and armatures using surface active substances “

Chemistry in the Oil Industry XIV
Session 8: Flow Assurance

19 November 2015; Florian Stephan Merkel, Heyko Jürgen Schultz, Carsten Schmuck

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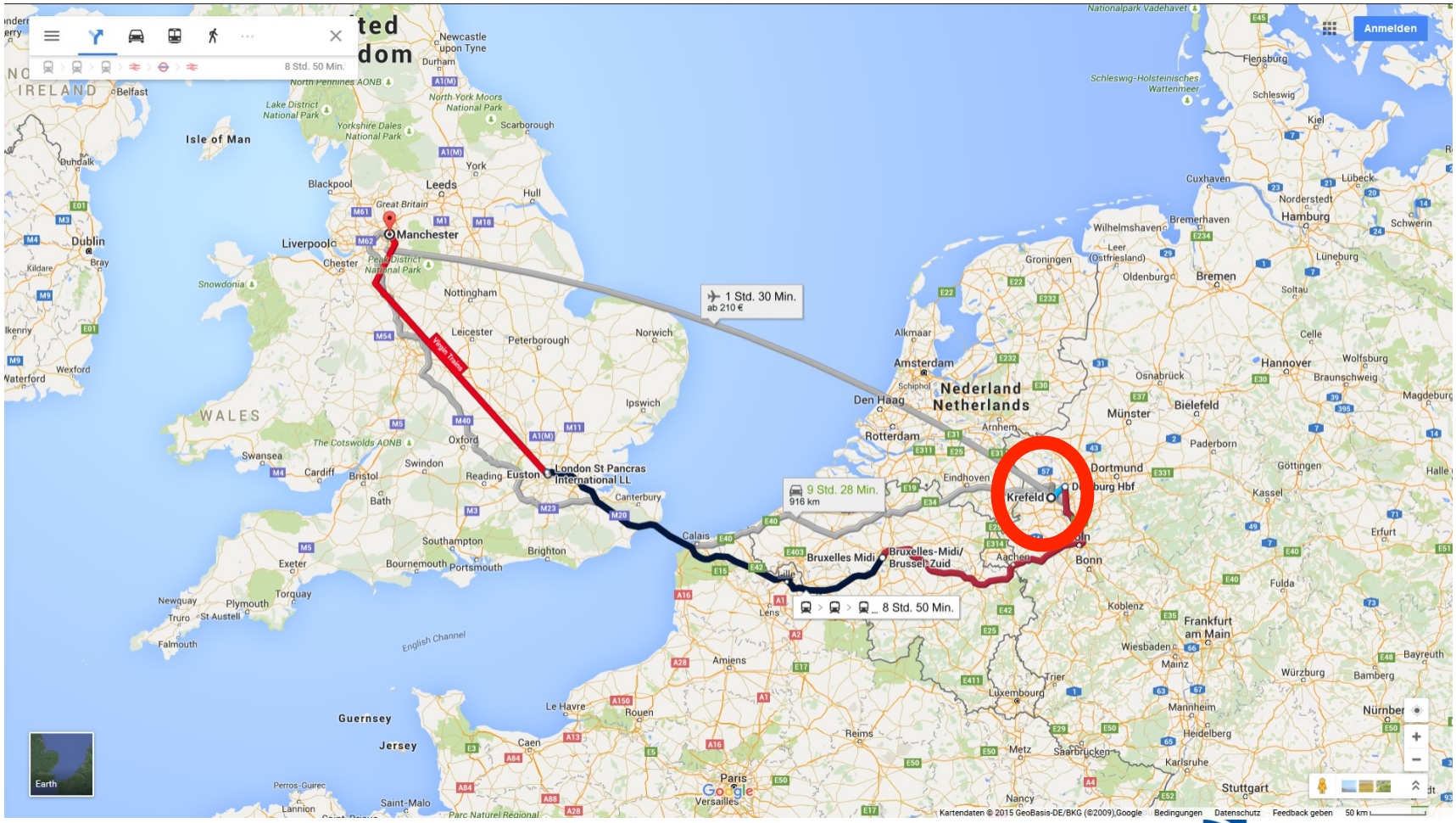
Outline

1. Introduction
2. Theoretical background
3. Approach of project “InHydRo”
4. Experiments / Experimental design
5. Results & discussion
6. Conclusion & outlook

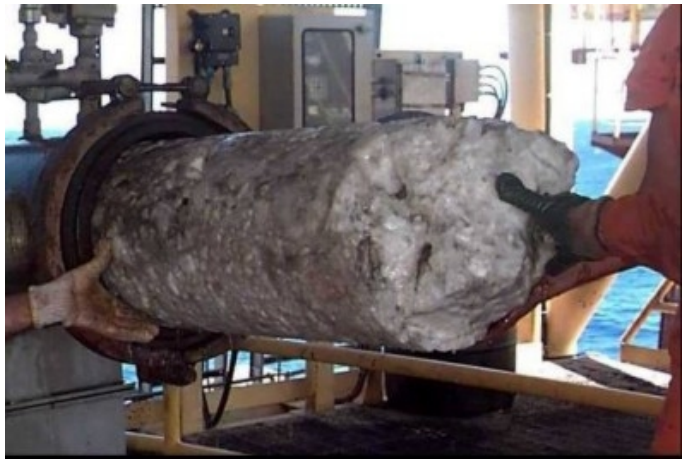
1. Introduction
Schultz group



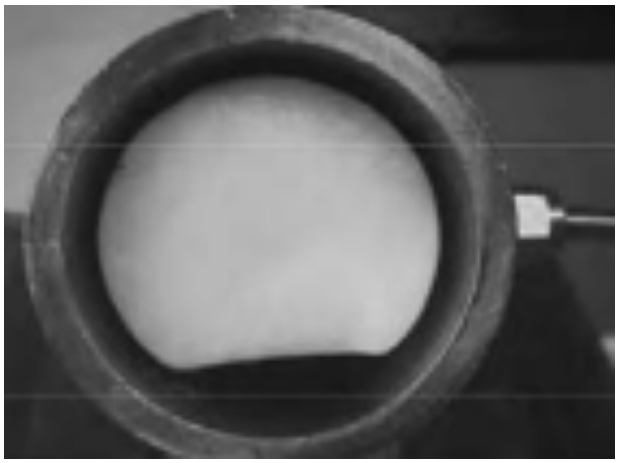
1. Introduction
What are clathrates / hydrates?

- Lat. „clatratus“: barred
- Inclusion compounds made of host and guest molecules (like CH_4, CO_2)
- Host = water → also called „Hydrates“
- Ice-like compounds
- Form at high pressures and low temperatures

→ Problematic in pipelines (especially sub-sea or in permafrost regions); causes „Plugging“



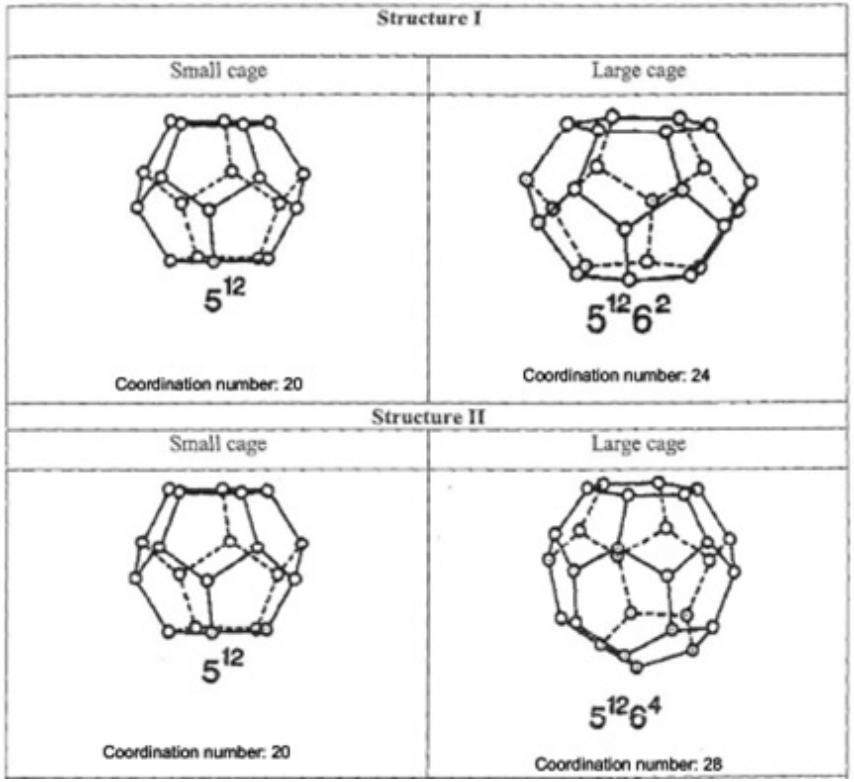
Source: Institute of petroleum engineering



Source: Sloan

2. Theoretical background
Structure of gas hydrates

	Structure I		Structure II	
Number of water molecules per unit cell	46		136	
Cage description/ notation	5^{12}	$5^{12}6^2$	5^{12}	$5^{12}6^4$
Labeling	U	V	U	W
Number of cages per unit cell	2	6	16	8
Coordination number z_i	20	24	20	28
Composition (theoretical / ideal)	2 U * 6 V * 46 H_2O		16 U * 8 W *136 H_2O	
Hydration number n	5,75		5,67	



Source: Schultz

Source: Khalik

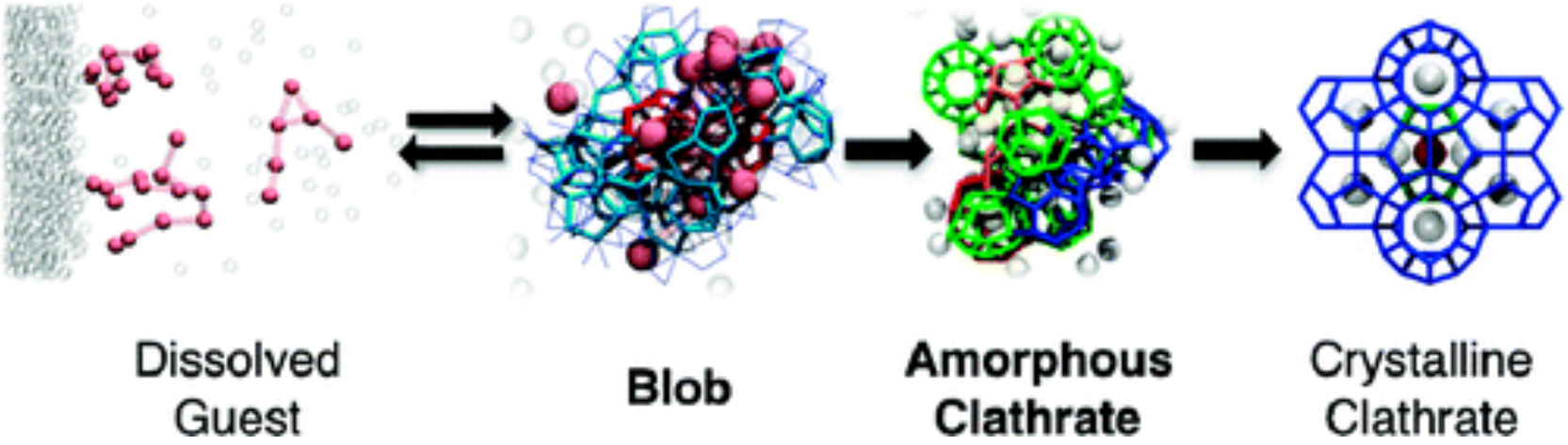
2. Theoretical background
Formation of gas hydrates

- 2 Phases (similar to crystallization):
  - Nucleation phase
  - Growth phase

- Nucleation
  - For a long time: Labile cluster theory (Sloan, Christiansen)
  - Today, there are different theories:
    - Nucleation at the interface
    - Local structuring nucleation
    - Amorphous intermediate structures (“Blobs”)

Actual mechanism remains unexplained to this day!

2. Theoretical background
“Blob” theory



Source: Jacobson

2. Theoretical background
Formation of gas hydrates

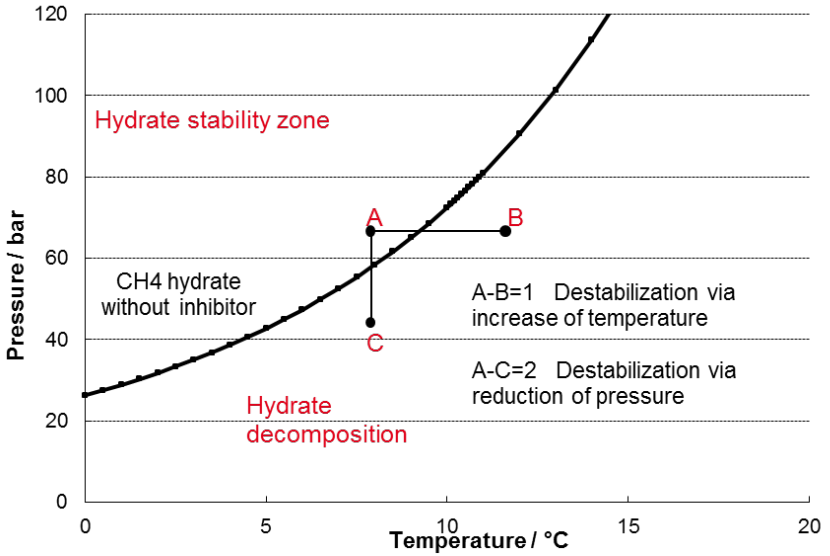
Important in all theories:

- **Contact between gas and water phase is critical for hydrate formation**
- **Higher turbulence leads to higher hydrate formation rate**
- **Most important parameter for determining inhibitor performance:**
  - **Induction time (time between start of experiment and onset of macroscopic hydrate formation)**
- **Induction times are stochastic with limited predictability for hydrate onset**

→Large number of experiments needed (for statistically significant predictions)

2. Theoretical background
Inhibition of gas hydrate formation

- **Physical inhibition**
  - **Reduction of pressure**
  - **Increase of temperature**
  - **Removal of water**
- **Chemical inhibition**
  - **Thermodynamic Hydrate Inhibitors (THI)**
  - **Low Dosage Hydrate Inhibitors (LDHI)**
    - **Kinetic Inhibitors (KHI)**
    - **Anti-Agglomerants (AA)**



Source: Figlhuber

3. Approach of project “InHydRo” Inhibition via surface active substances

Idea

- **Conventional inhibitors have to be dosed in the pipeline permanently and have to be separated again after leaving the pipeline → expensive, bad for environment**

- **Plugging in pipelines often occurs in places, where there is a change in flow geometry (bends, valves, …)**

- **Development of a hydrate-inhibiting coating, which can be applied to the pipeline in critical regions, seems very promising to solve the plugging problem**

4. Experiments
“Pillars” of project InHydRo

1. A new and innovative method to determine the inhibition suitability of the substances in a reliable and accurate way was developed.

2. Screening of substances/research on inhibition suitability for structure II (sII) inhibition has been conducted. Experiments took / take place at pressures <10 bar. Additionally, possible inhibitors have been synthesized and tailored.

3. “Optimal” parameters (pressure, temperature, type of stirrer, …) for high pressure experiments (to determine sI inhibition suitability) have been determined in extensive experimental series.

4. After the determination of optimal parameters, a high-pressure screening of substances for sI inhibition suitability took place.

4. Experiments
“Pillars” of project InHydRo

5. Parallel to the experiments, kinetic analyses of the high pressure experiments were conducted. The focus/goal of this analyses was to gain in-depth knowledge of the formation mechanism and to develop a predictive model to allow better inhibitor performance evaluation.

6. Gas hydrate structures have been determined via RAMAN-spectroscopy.

7. The whole project is undergoing permanent audits and evaluation as well as optimisation to ensure the best possible accuracy of results.

4. Experiments
Procedure for determining sII inhibition suitability

- sII screening takes place in IKA LR 2000 system

- Experimental procedure:

  - Water/THF-mixture (molar ratio 17:1) is given into reactor. THF acts as a promoter, accelerates the screening and ensures sII hydrate formation
  - Inhibitor is given into reactor (varying conc. of 1, 3 and 5 %(wt.)); reactor is closed
  - Reactor is tempered to 20 °C ± 0,5 °C (with stirrer set to 50 min^{-1})
  - Reactor is purged with methane (with stirrer off)
  - Reactor is filled with methane
  - Reaching of target pressure is set as starting point of experiment
  - Stirrer is set to 50 min^{-1}, temperature is set to target value

A sign for onset of hydrate formation is a decrease in pressure with parallel increase in temperature (because enthalpy of formation is about -57 kJ /mol).

4. Experiments
Procedure for determining sI inhibition suitability

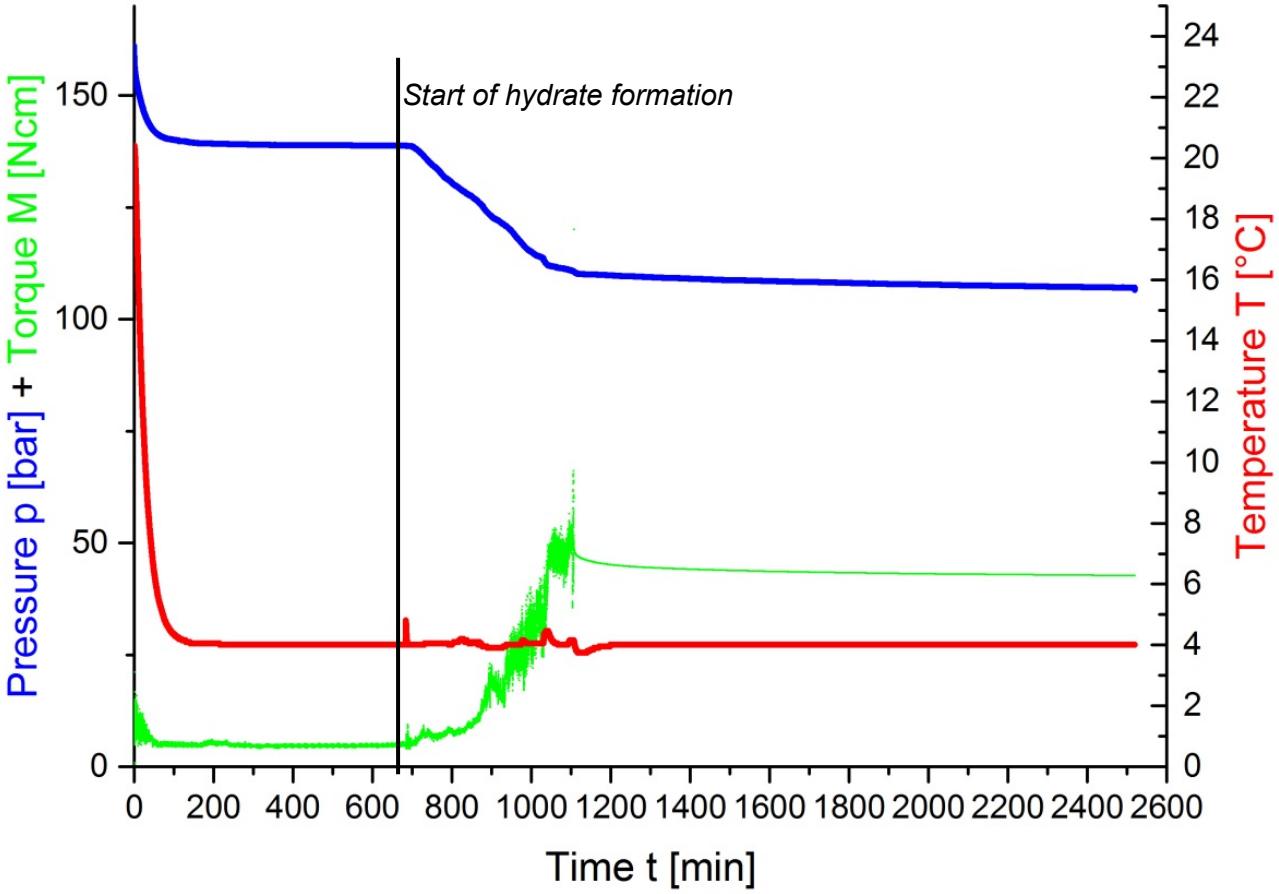
- **sI screening takes place in Parr 4568 reactor**

- **Experimental procedure:**

  - **Water (249,5 g ± 0,5 g) and inhibitor (varying conc. of 1, 3 and 5 %(wt)) are given into reactor; reactor is closed**
  - **Reactor is tempered to 20 °C ± 0,5 °C (with stirrer set to 200 min^{-1})**
  - **Reactor is purged with methane (with stirrer off)**
  - **Reactor is filled with methane (via Coriolis-Mass-flow-meter)**
  - **Reaching of target pressure is set as starting point of experiment**
  - **Stirrer is set to 200 min^{-1}, temperature is set to target value**

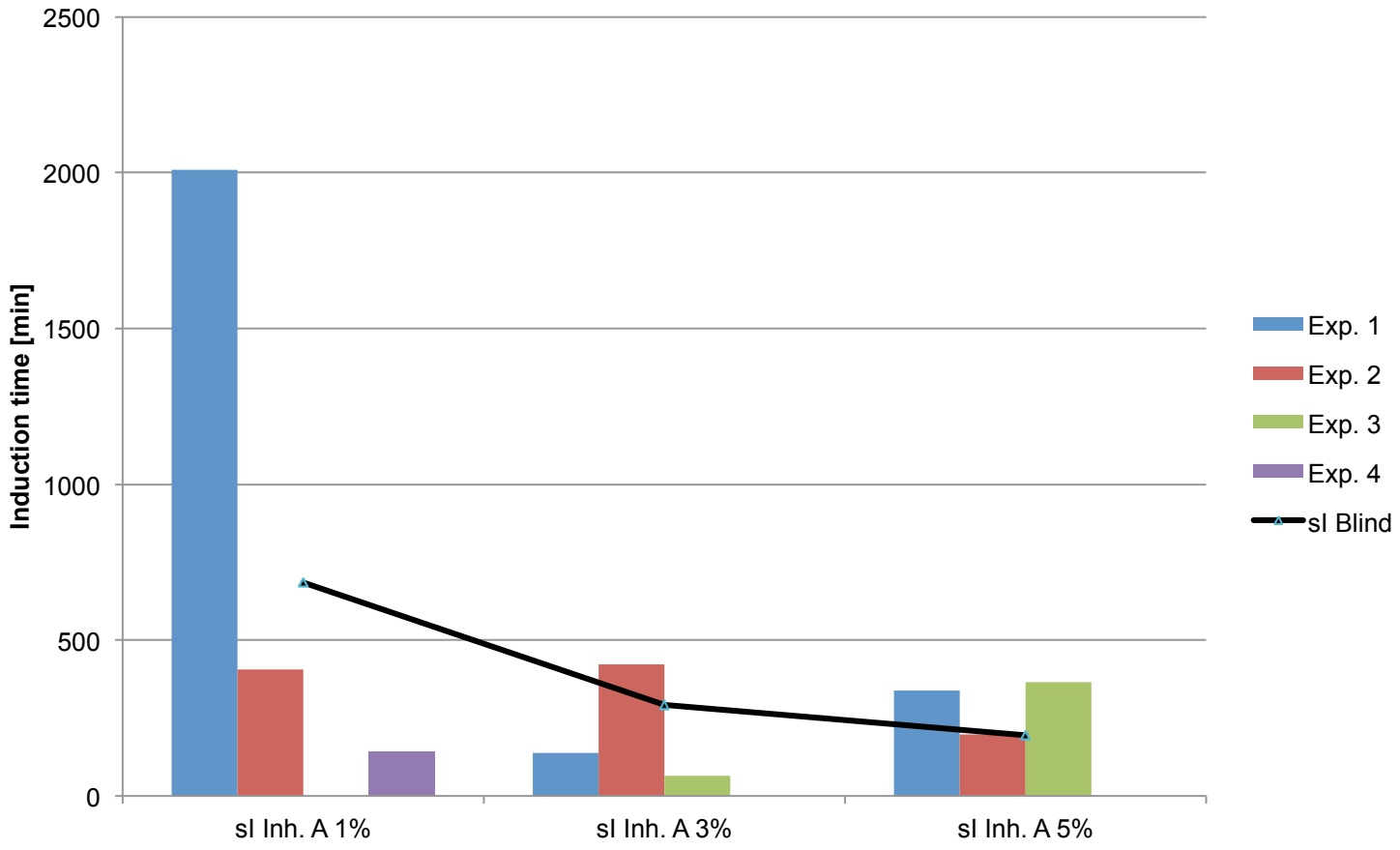
A sign for onset of hydrate formation (“induction time”) is a decrease in pressure with parallel increase in temperature (because enthalpy of formation is about -57 kJ /mol).

5. Results & discussion



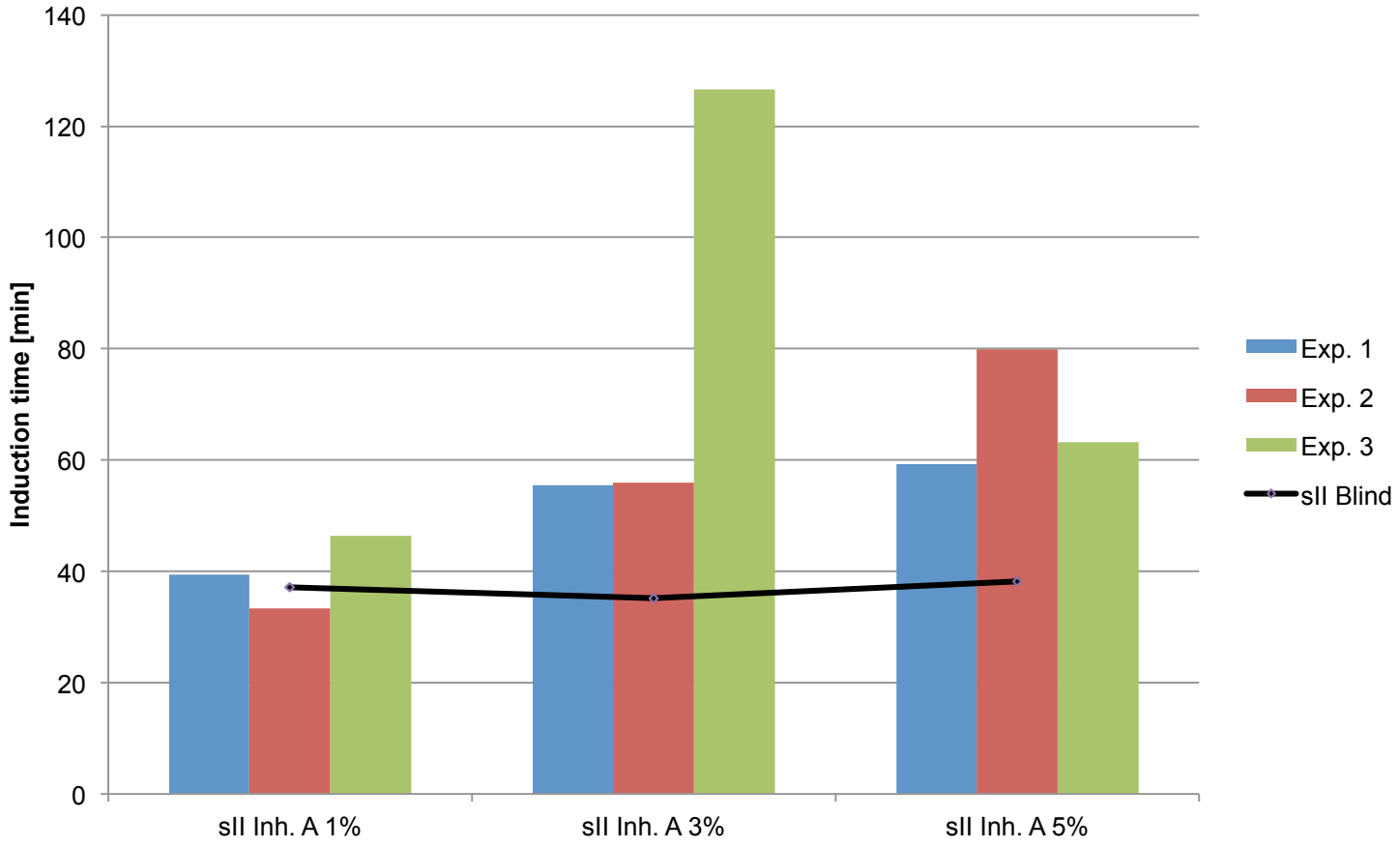
Sample hydrate formation experiment, no inhibitor

5. Results & discussion



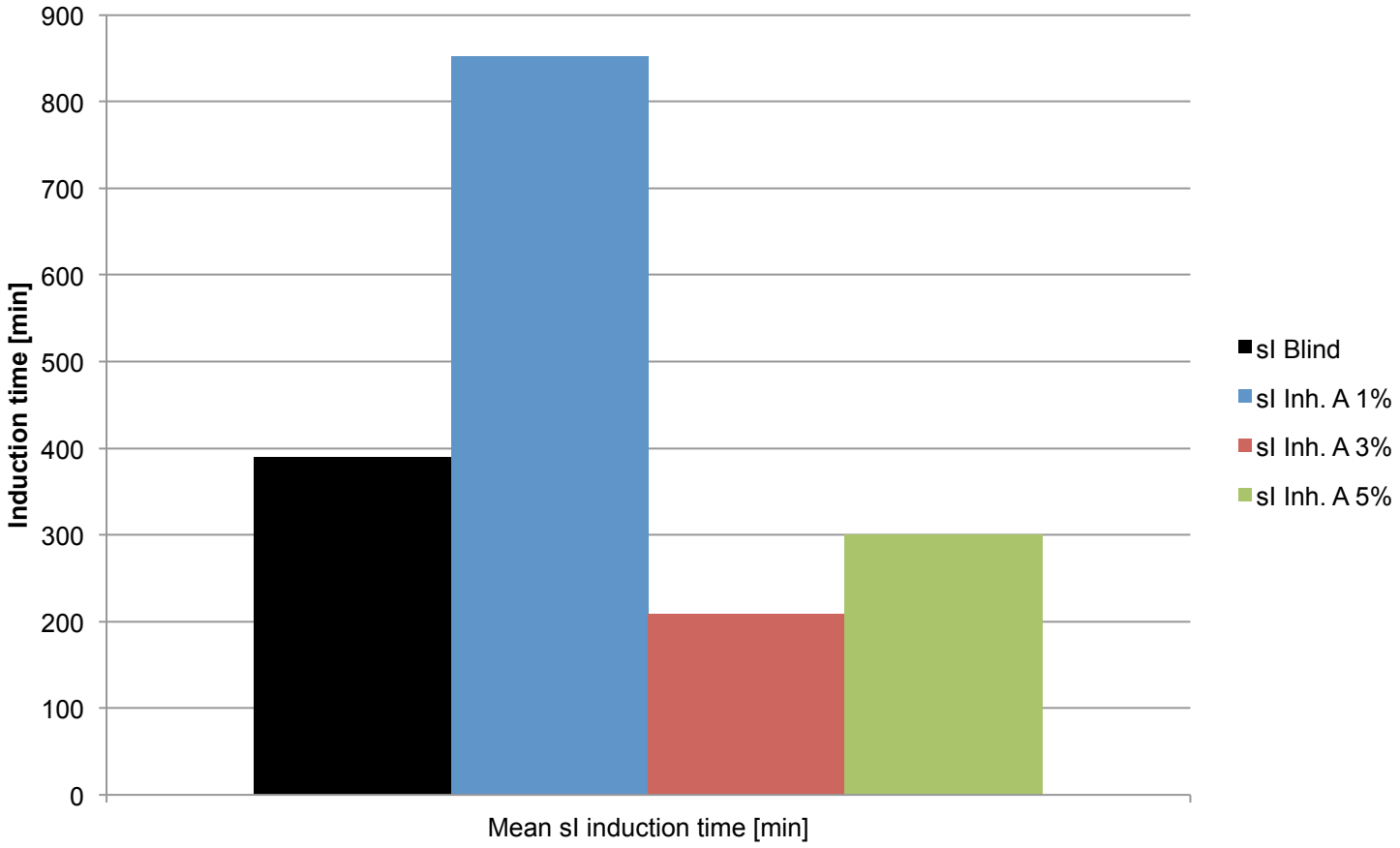
Induction times of chosen experiments, Inhibitor A, sI inhibition

5. Results & discussion



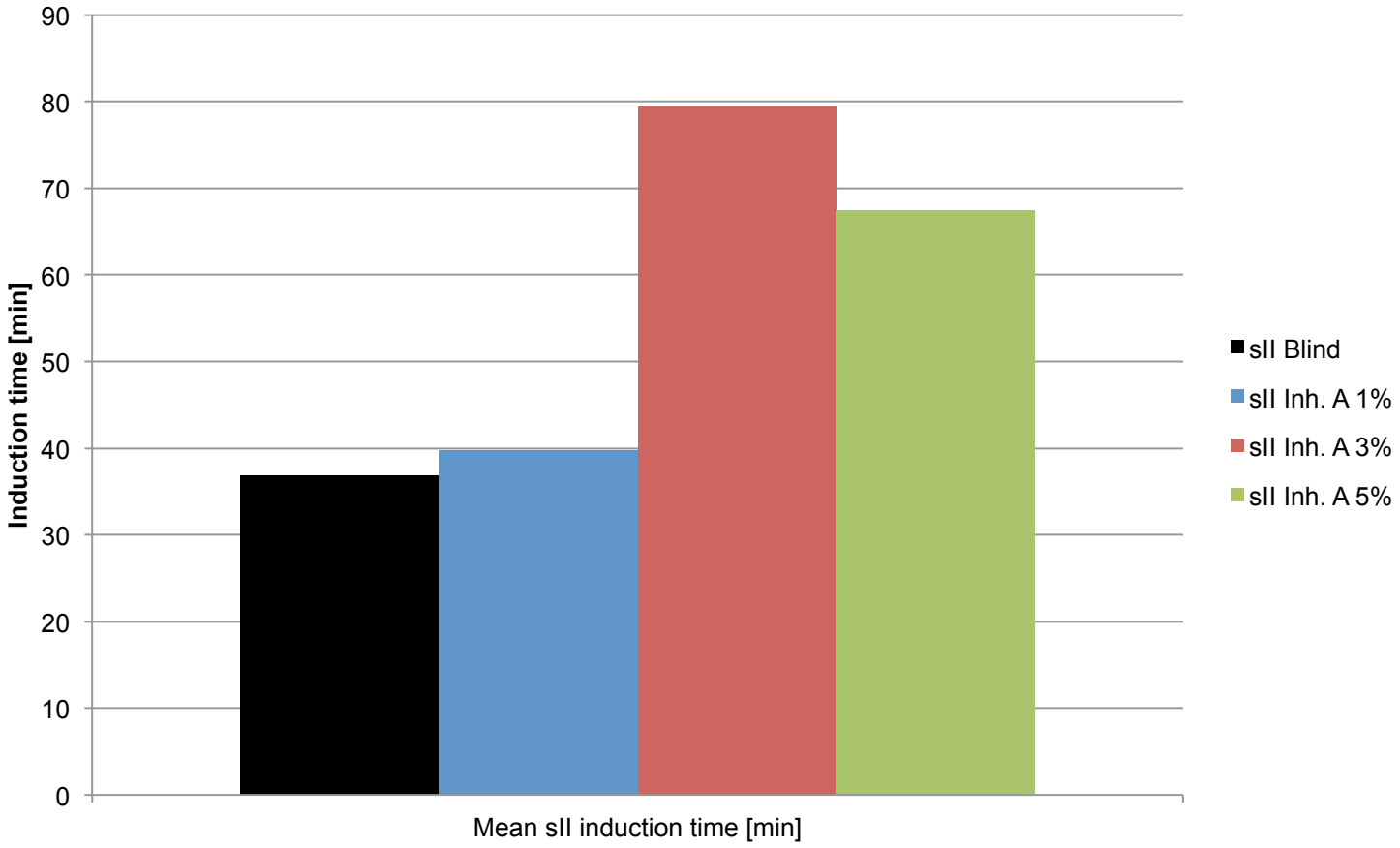
Induction times of chosen experiments, Inhibitor A, sII inhibition

5. Results & discussion



Comparison of mean sI induction time

5. Results & discussion



Comparison of mean sII induction time

6. Conclusion & Outlook

- Examination of surface active substances is feasible with developed method
- The importance of concentration effects is shown
- Up to date no „perfect“ inhibitor has been found; „good“ sII-inhibitors are not automatically „good“ sI-inhibitors → Screening on-going; alternatively, two inhibitors included in one coating
- Kinetics are describable, but hydrate forming mechanism has to be further elucidated for developing a complete mathematical model
- Induction times have been examined under various statistical aspects (normality, Dixon-Q, ANOVA,…)

6. Conclusion & Outlook

Experiments are a good starting point for deepening research:

- **Optimisation of the discovered substances in regards to the inhibition of both hydrate structures**
- **Examination of further possible inhibitor candidates**
- **Further variation of inhibitor concentration (< 1 %(wt.))**
- **The development of an inhibiting surface is following two parallel tracks:**
  - **Application of promising inhibitors as a coating and development of a coating „primer“ to fixate inhibitors on a defined substrate**
  - **Further elucidation of the hydrate formation mechanism with various analytical methods (Raman, High-speed camera system, …)**

Thank you for your kind attention!

Questions?

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Florian Stephan Merkel

Chemische Technik / Chemical Engineering

Hochschule Niederrhein / University of Applied Sciences Niederrhein

Fachbereich 01-Chemie / Faculty of Chemistry

Raum S E20 / Room S E20

Adlerstr. 32

47798 Krefeld, Germany

Tel.: +49 2151 / 822 - 4041

Fax: +49 2151 / 822 - 4013

florian.merkel@hs-niederrhein.de


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Experiments

Accuracy of measurements, Parr 4568

Parameter	Sensor	Accuracy
Temperature T	Juchheim PT100	0,3 to 0,8 % of measured value (at experimental temperatures)
Pressure p	Ashcroft OEM-pressure transducer G2	±2 bar
Pressure p (after optimization)	Emerson Rosemount 2088	0,10 % of measured value
Agitator torque M	Parr DR-2500	0,10 % of measured value
Mass m	Sartorius LE1003	±0,001g
Conductivity	Inolab-cond 740	±1% of measured value