H_2S Scavenger Qualification for Subsea Applications

DNV GL Offshore Pipeline Day

Feb. 24, 2020

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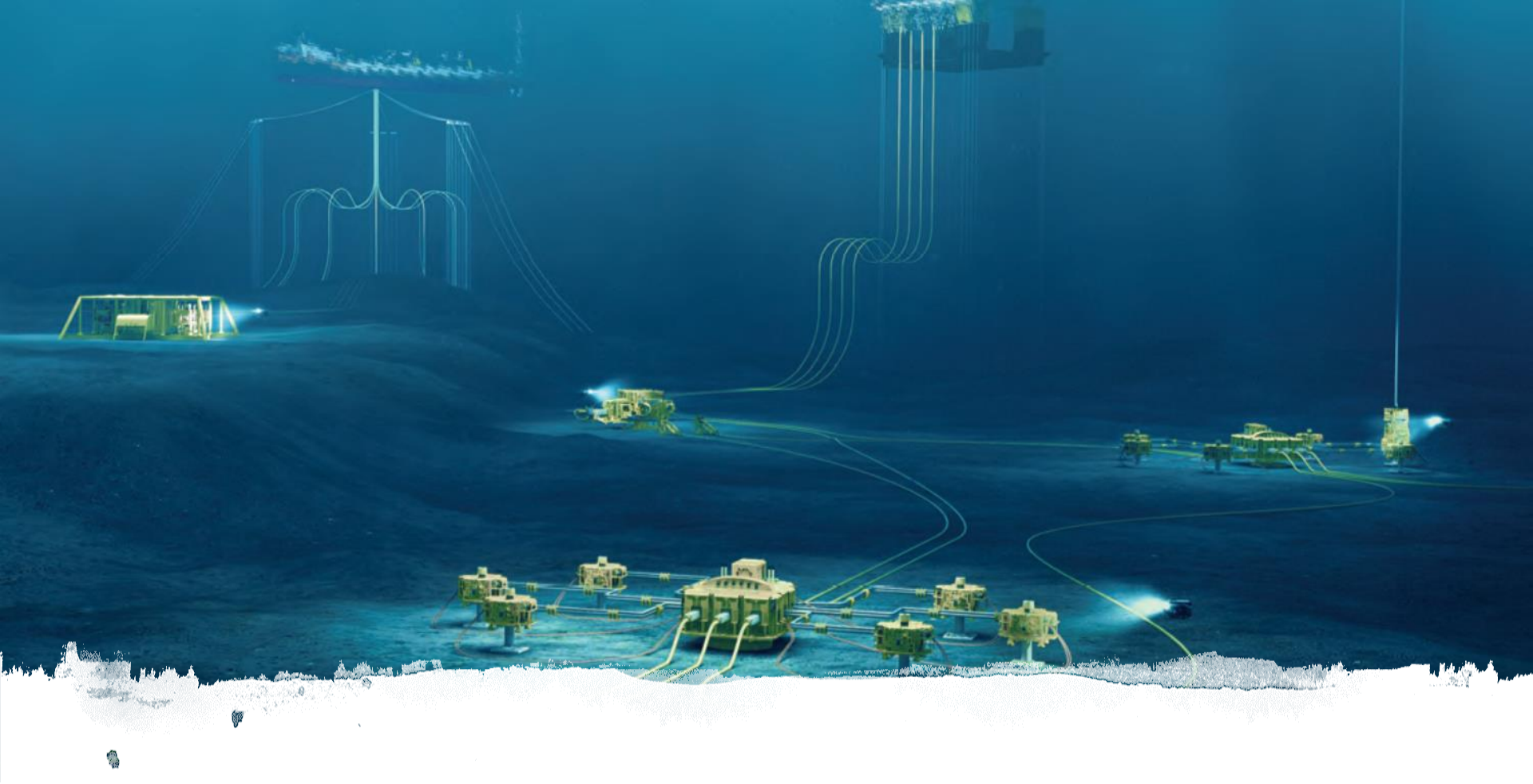

Outline

- Introduction
- Laboratory Performance Tests
- Compatibility Tests
- Field Trials

H_2S Scavenger Selection and Qualification for Subsea Application

- Injection of liquid H_2S scavengers is an alternative to control H_2S concentration and mitigate its effects
- Liquid scavengers react with H_2S to form stable water- or oil-soluble products
- Many chemical products are now available. This study was initiated with Triazine based products
- There was no industry-recognized methodology to qualify scavengers, mainly for multiphase applications
- In some cases, not only the efficiency of the product is important, but also the kinetics.
  - For example, it may be required that the H_2S be reduced below a certain level before the fluid reaches materials that are not designed for sour service.
- In addition to H_2S scavenging performance tests, these chemical products need to be qualified for capillary or umbilical injection and their compatibility with other chemicals injected evaluated.

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H_2S Scavenger Qualification Laboratory Methodology

- C. Mendez, A. Magalhaes, J. Vera, P. Altoe, E. Costa Bastos. New Methodology and Testing Systems for Evaluating H_2S Scavengers' Efficiency at Simulated Field Conditions. Latincor 2012.
- C. Mendez, J. Vera, A. Magalhanes, P. Altoe, E. Costa Bastos. Development of a Novel Testing Protocol and equipment for the Evaluation of H_2S Scavengers. NACE International CORROSION/2012. Paper C2012-0001466. 2012

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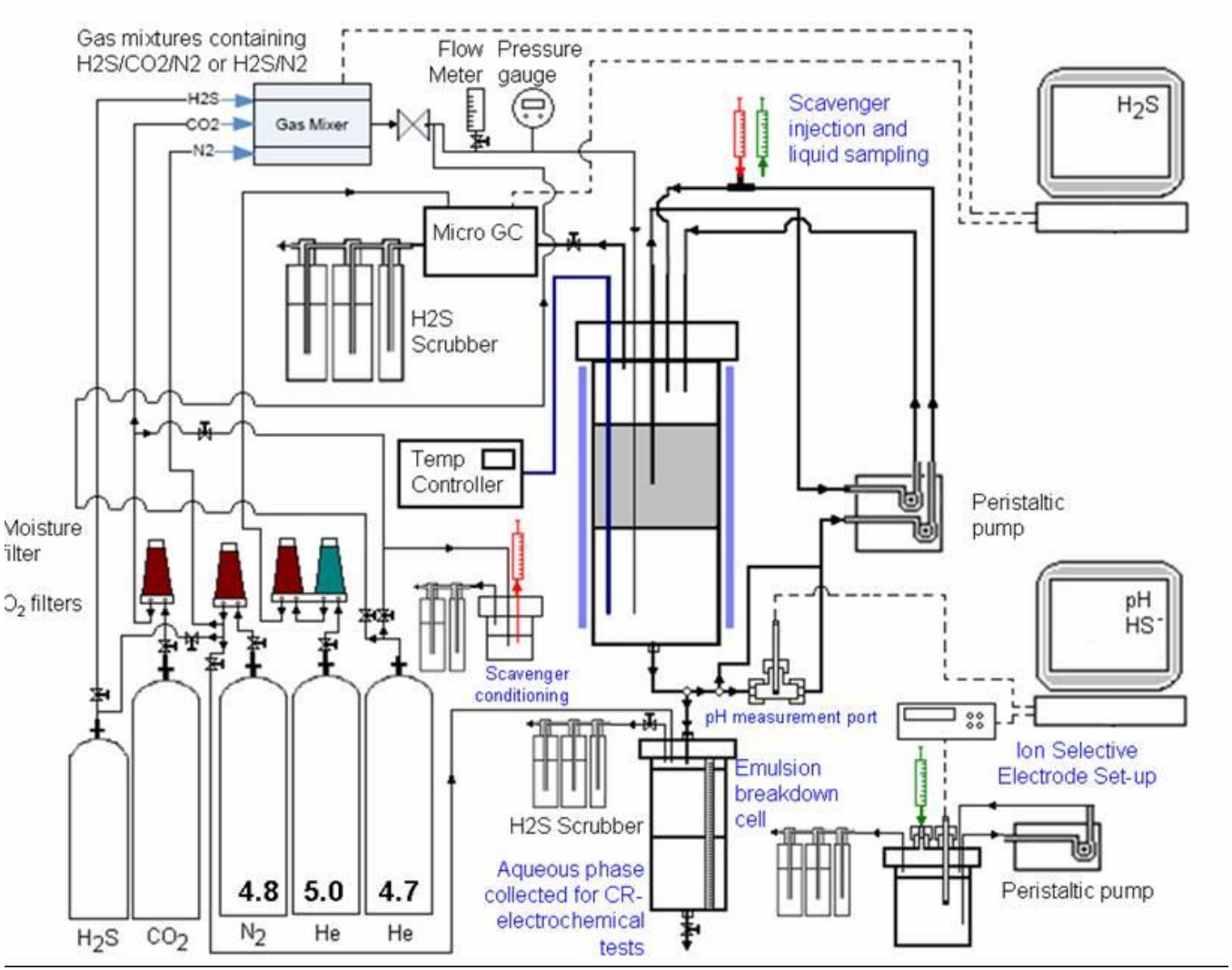
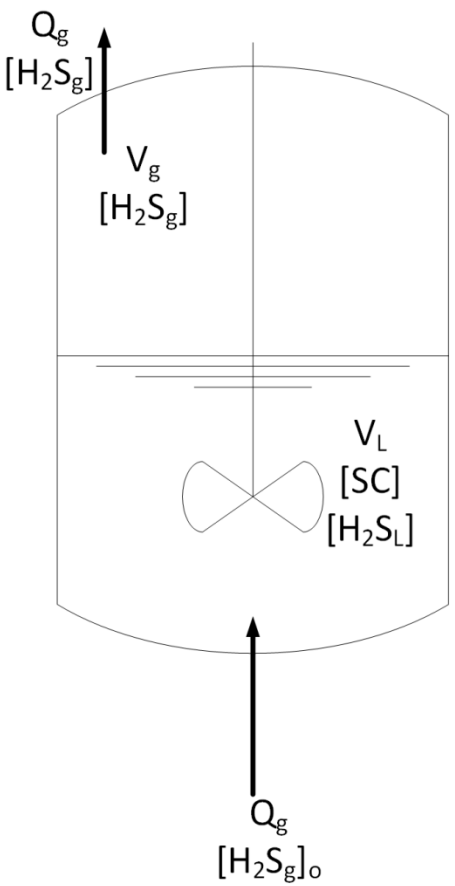
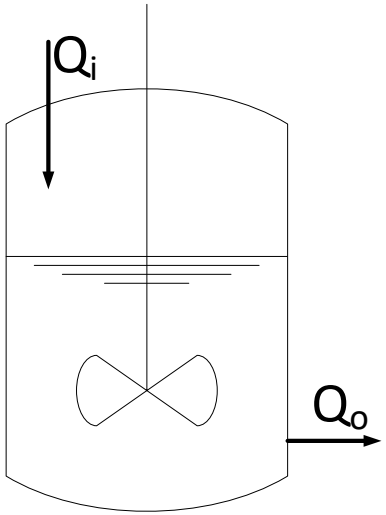
Semi-batch Test Set-up
CSTR with continuous gas replenishment





Introduction
CSTR Basics



- The Continuous flow Stirred-Tank Reactor (CSTR) is an ideal reactor type commonly used in chemical engineering to study reaction kinetics.
- The set-up requires a continuous input and output of fluids. For practical reasons, the volumetric flow rates at inlet and outlets are the same (i.e., $Q=Q_i=Q_o$)
- The mathematical model can be easily derived assuming a perfect mixing within the reactor, so that the composition of the fluid getting out is equal to the composition inside the reactor.
- The model is based on mass balance and works for all fluids: liquids, gases, and slurries. For a component *i* entering the reactor with a concentration C_i and exiting with C_o

$$\textit{Accumulation Rate of } i = Q_i\, C_i - Q_o\, C_o + \textit{Generation Rate of } i$$

Introduction
CSTR Advantages

- Continuous replenishment
  - Facilitates the control of species in the reactor, which affect reactions related to corrosion processes.
  - Allows continuous measurement of fluid compositions, without affecting the area/volume ratio
- Provides additional kinetic data that can be used to
  - Better understand reaction mechanisms and interactions among variables
  - Improve test methodologies
  - Develop predictive models

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H_2S Scavenger Kinetics (for a water soluble Triazine scavenger)

- Step 1: transport of the liquid scavenger into the aqueous phase, with partitioning to the oil phase. Assumed to be scavenger and mass transport dependent, but H_2S independent.

$$C_3R_3N_{3(aq)} + H^+ \underset{k-4}{\overset{k4}{\rightleftharpoons}} C_3R_3N_3H^+$$

- Step 2: transport of H_2S from the gas and crude oil phases into the aqueous phase. Assumed to be H_2S and mass transport dependent, but scavenger independent. Total dissolved sulfur species are pH dependent.

$$H_2S_{(g)} \underset{k-1}{\overset{k1}{\rightleftharpoons}} H_2S_{(aq)} \qquad H_2S_{(aq)} \underset{k-2}{\overset{k2}{\rightleftharpoons}} HS^- + H^+$$

- Step 3: chemical reaction between the scavenger and dissolved H_2S. Assumed that the dissolved triazine-based scavenger ($C_3R_3N_3$) reacts irreversibly with the dissolved H_2S to produce stable water-soluble products. This homogeneous reaction was considered as scavenger and $H_2S_{(aq)}$ dependent, but mass transport independent.

$$HS^- + C_3R_3N_3H^+ \xrightarrow{k_3} C_3R_2N_2S + RNH_2$$

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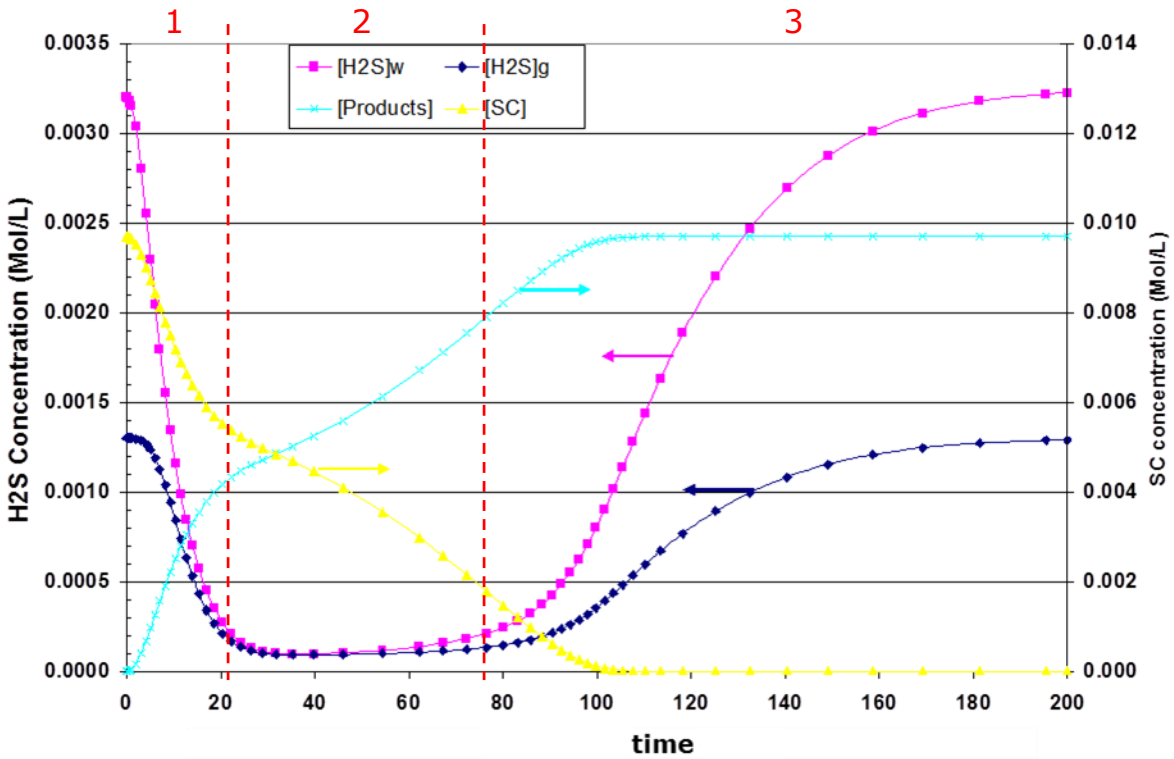
Pre-screening Test – Kinetic Model



- Semi-batch reactor with DI water pre-saturated with H_2S
- H_2S/N_2 gas mixture continuously purged at 1 mL/min
- Fixed volume of scavenger injected at time = 0 (0.07 ppm SC in water/ppm H_2S in the gas).
- Three regions in transient:
  1. $[H_2S]g$ decrease. Related to the scavenger kinetics and mass transport.
  2. $[H_2S]g$ plateau. Minimum and duration related to gas flow rate and initial $[H_2S]g$, scavenger efficiency (and concentration).
  3. $[H_2S]g$ increase. Mainly related to the mass transfer controlled dissolution of H_2S from gas to the liquid.

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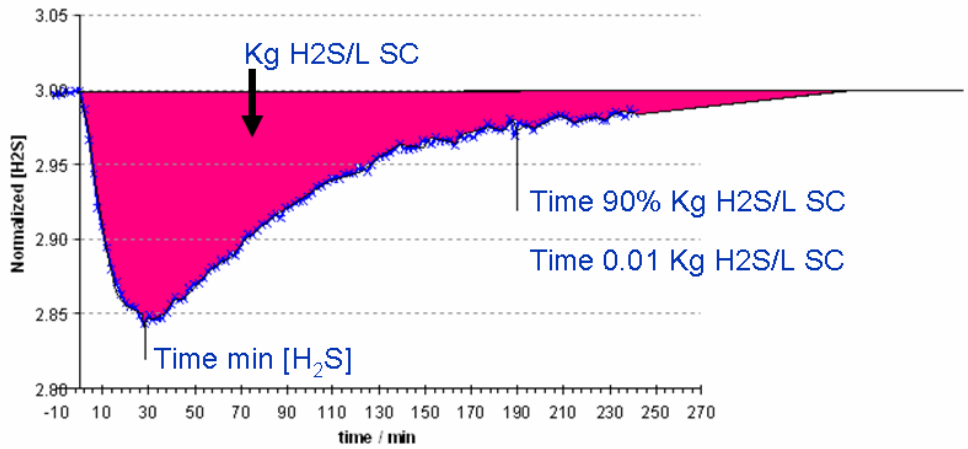
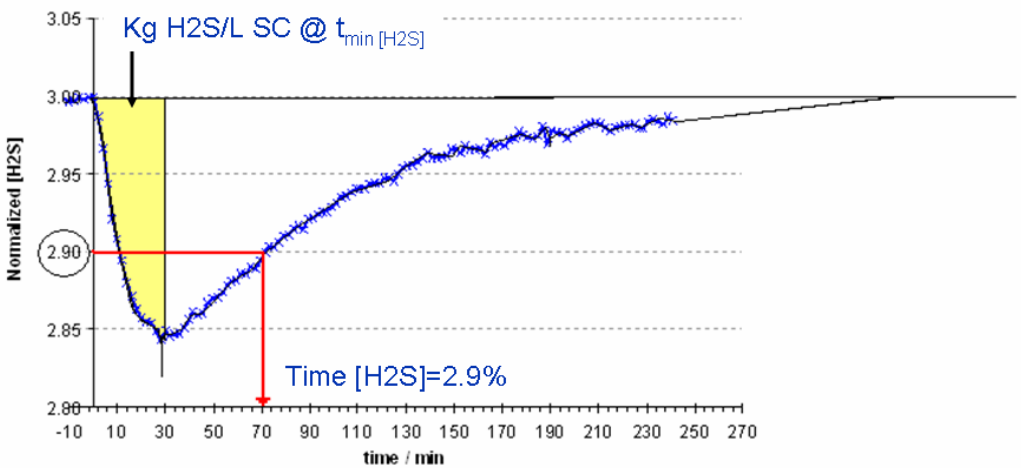
Semi-batch Test
Parameters selected for data interpretation





- From the transients, reaction kinetics and SC performance can be obtained
- Few parameters selected for screening SC or evaluating effect of different parameters

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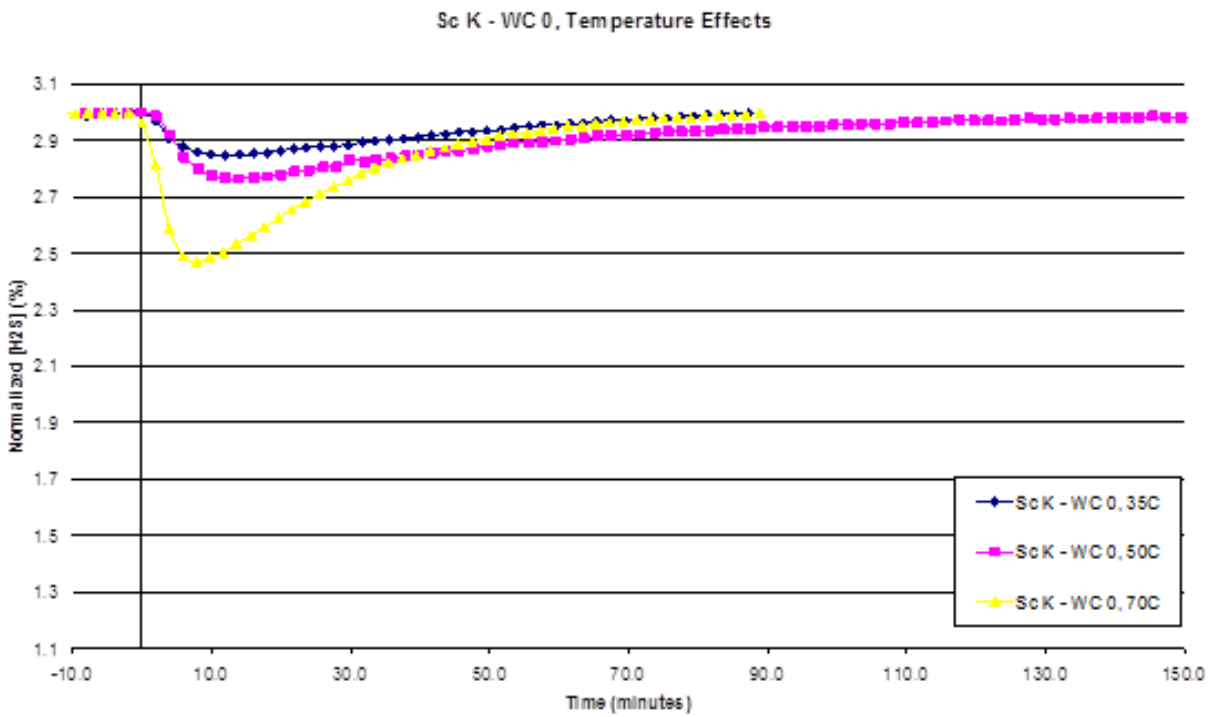
Pre-screening Test
Temperature Effect



- Evaluated performance of different chemicals and the effect of parameters such as brine composition and pH, temperature, type of crude oil (TAN, viscosity) and water cut, presence of other chemicals (scale inhibitor, demulsifier)

H_2S Scavenger Selection and Qualification Summary

- A novel test methodology and systems were developed and implemented to evaluate the efficiency of liquid H_2S scavengers at oil and gas simulated production conditions. This methodology is still being routinely used.
- Approach gives an overall picture of a scavenger performance
  - initial screening of chemicals performance under different conditions
  - reaction kinetics at high P/T and multiphase flow conditions
- The performance of several commercial products was characterized not only by the efficiency in removing H_2S from the gas phase when injecting to a multiphase flow, but also in terms of the kinetics of the reaction.
- A simplified kinetic model was developed with the objectives of
  - understanding the effect of different parameters in the H_2S scavenging reaction
  - assisting in the design of an experimental setup and test matrix that could produce data useful not only for evaluating products in the laboratory but also for helping optimize chemical treatment in the field.

H_2S Scavenger Qualification
Compatibility tests

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H_2S Scavenger Compatibility Tests

- H_2S scavengers to be injected subsea should be certified for subsea application, to prevent potential plugging of capillary and umbilical (API Tech. Report 17TR6).
- Tests typically conducted by chemical suppliers include:
  - Viscosity and density at temperature/pressure corresponding to the facility, subsea and (if needed) well conditions.
  - Solvent characteristics
  - Particulate content
  - Temperature stability
  - Hydrate stability
  - Compatibility tests with metallic and polymeric materials that may get in contact with the neat chemical

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Compatibility Tests
H_2S Scavenger – Other fluids

- Different fluid-fluid compatibility tests need to be conducted depending on the application
  - During umbilical commissioning: Neat scavenger compatibility, at different temperatures, with
    - chemicals that may have been in the umbilical before commissioning (e.g., corrosion inhibitor, demulsifier, scale inhibitor, biocide)
    - Spacer of barrier fluids that may be used for displacement of existing chemicals (e.g., EGMBE, naphtha, diesel, methanol, xylene)
  - During scavenger application: Fresh and spent scavenger compatibility with produced fluids in the production tubing, pipeline or in the umbilical (e.g., injection open port may experience backflow of produced fluids, component failure)
    - Produced oil/condensate samples
    - Gas composition (e.g., CO_2)
    - Brine composition

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H_2S Scavenger Qualification
Field Evaluation in Multiphase Subsea System

- **J. R. Vera, C. Mendez, H. Suarez. Field Evaluation of H_2S Scavenger Efficiency Injected in a Multiphase Subsea System. NACE International CORROSION/2016. Paper C2016-7545, 2016**

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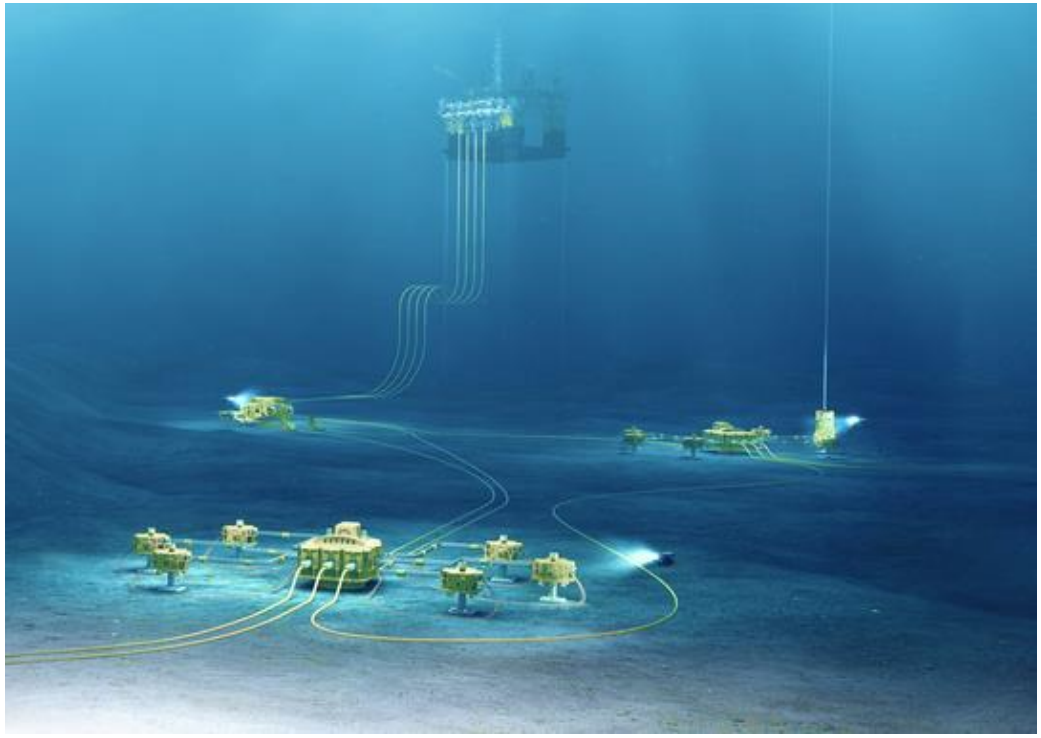
Subsea Field Trial

- H_2S scavenger reported to have between 10 and 30% w/w of triazine, with a capacity of 0.76 mole H2S /mole triazine
- H_2S Scavenger injected at subsea wellhead
  - H_2S concentration measured at the test separator connected to the flowline transporting fluids from the well being tested
  - 2-3 hours allowed between scavenger dosage changes and H_2S testing



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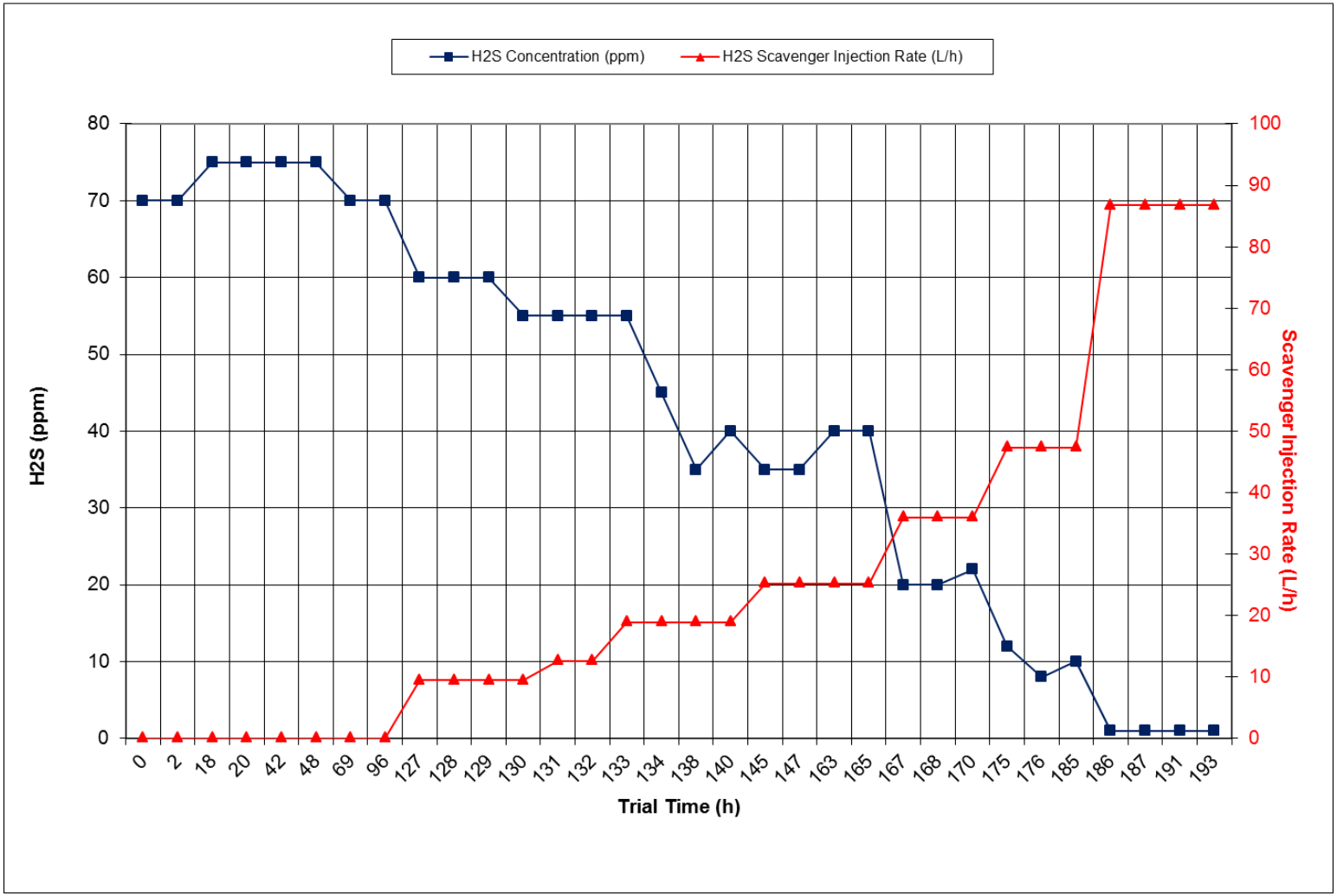
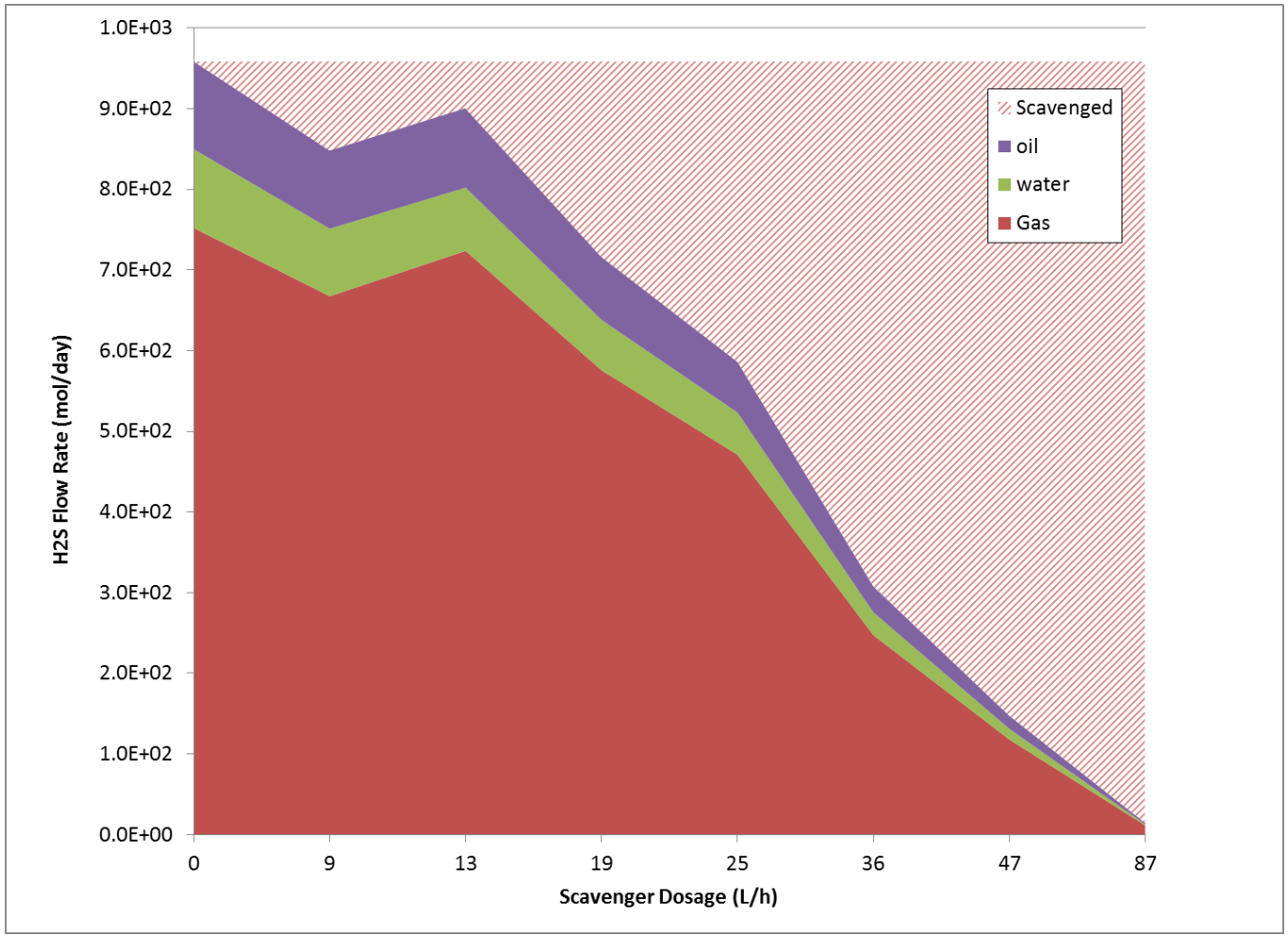
H_2S Concentration and Scavenger Dosage during Field Trial



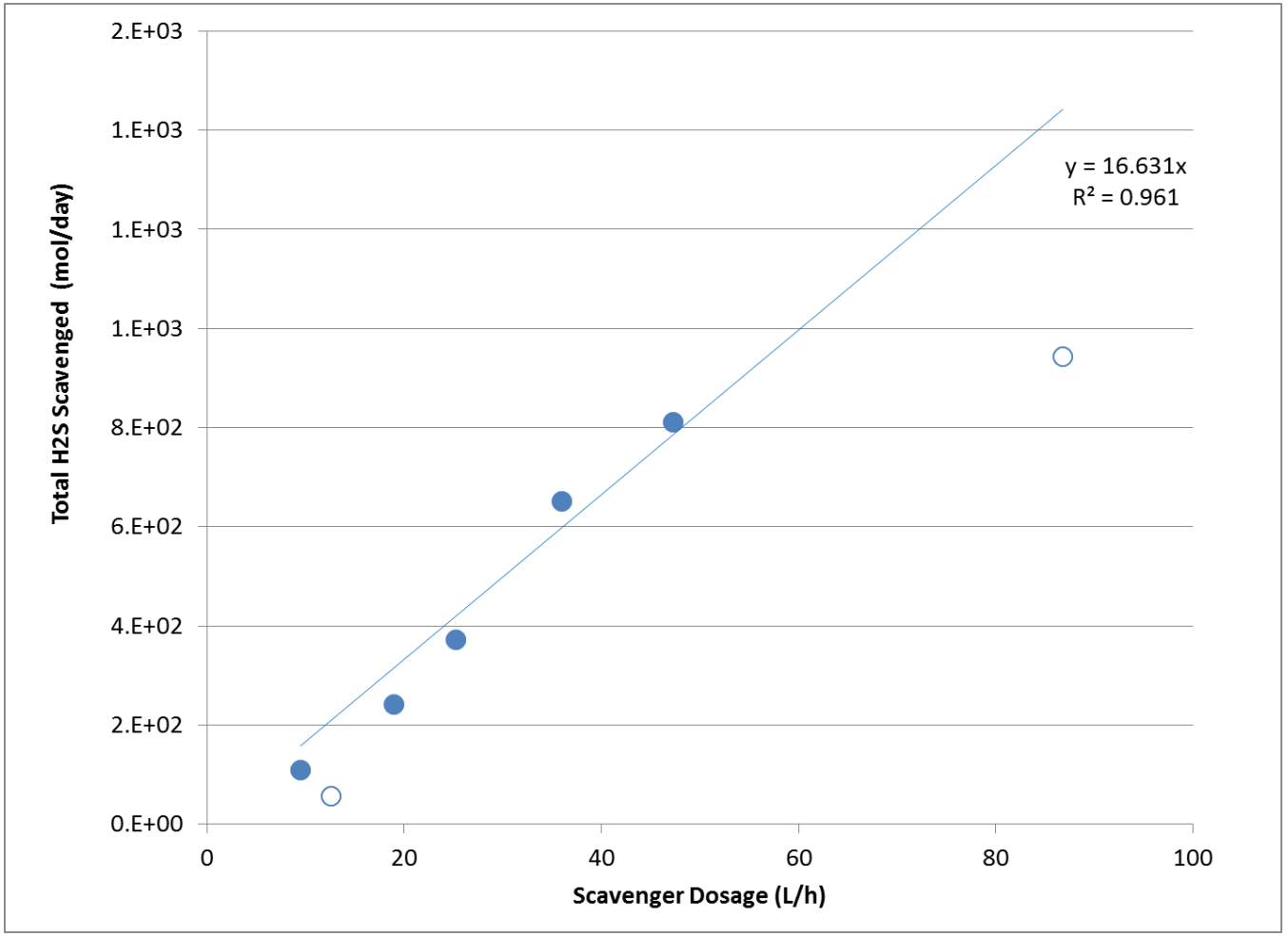
- H_2S concentration reduced below DL at a dosage of 87 L/h (550 GPD)

H_2S Molar Flow Rates during Field Trial



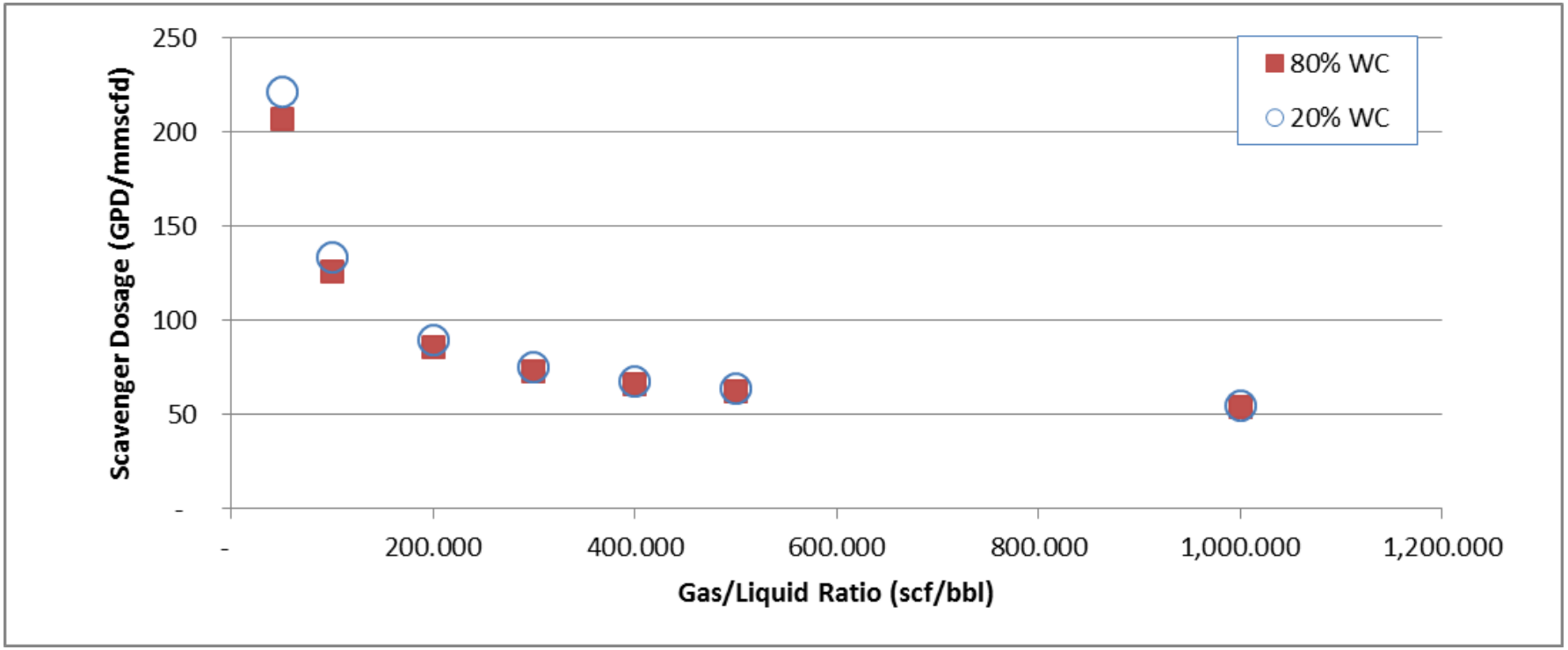
- H_2S content of multiphase streams calculated using OLI Analyzer based on
  - H_2S concentration gas measured at topside separator
  - gas and liquid compositions
  - operating conditions
- At these GLR, water cut and pH values, H_2S molar rate in the gas phase dominated

Effect of Scavenger Dosage on Total H_2S Reacted



- Average scavenger capacity: 0.693 mol H2S/L SC (2.62 mol H2S/gal SC)
- Open circles show data points not included in the regression

Effect of GLR on scavenger dosage required to reduce 100 ppm of H_2S from 1 mmscfd



- Empirical equation developed for the specific field conditions

$$GPD_{SC} = \frac{ppm_{H_2S}}{2E_{SC}[SC]}(1.20\ mmscfd + 0.237\ mbod + 0.204\ mbwd)$$

- Where $2E_{SC}[SC]$ = 2.623 mol H_2S/ Gal SC

H_2S Scavenger Field Evaluation Summary

- A comprehensive approach was developed to complement the limited understanding of a H_2S Scavenger performance for this particular subsea application
- The H_2S scavenger efficiency, calculated from field data, was similar to the value disclosed by the chemical supplier, assuming a triazine concentration slightly higher than 10%.
- A methodology was developed based on field trials to estimate the H_2S scavenger injection dosage required to reduce the H_2S concentration in the gas, for multiphase systems.
  - GLR was shown to have a significant impact in the scavenger dosage

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Thanks for Your Attention

Questions?

Jose Rafael Vera
Jose.vera@dnvgl.com
+ 1 281 396 1743

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