Opportunity and Technical Challenges of cEOR: A Surfactant Manufacturer's Perspective

Royal Society of Chemistry

Chemistry in the Oil Industry XIV

2-4 November 2015, Manchester, UK

J.R. Barnes, T. E. King and L. Pretzer

Shell Global Solutions International B.V. , Amsterdam, Netherlands and
Shell Global Solutions (US) Inc., Houston, TX, USA

DEFINITIONS & CAUTIONARY NOTE

Reserves: Our use of the term "reserves" in this presentation means SEC proved oil and gas reserves.

Resources: Our use of the term "resources" in this presentation includes quantities of oil and gas not yet classified as SEC proved oil and gas reserves. Resources are consistent with the Society of Petroleum Engineers 2P and 2C definitions.

Organic: Our use of the term Organic includes SEC proved oil and gas reserves excluding changes resulting from acquisitions, divestments and year-average pricing impact.

Resources plays: our use of the term 'resources plays' refers to tight, shale and coal bed methane oil and gas acreage.

The companies in which Royal Dutch Shell plc directly and indirectly owns investments are separate entities. In this presentation "Shell", "Shell group" and "Royal Dutch Shell" are sometimes used for convenience where references are made to Royal Dutch Shell plc and its subsidiaries in general. Likewise, the words "we", "us" and "our" are also used to refer to subsidiaries in general or to those who work for them. These expressions are also used where no useful purpose is served by identifying the particular company or companies. ''Subsidiaries'', "Shell subsidiaries" and "Shell companies" as used in this presentation refer to companies in which Royal Dutch Shell either directly or indirectly has control, by having either a majority of the voting rights or the right to exercise a controlling influence. The companies in which Shell has significant influence but not control are referred to as "associated companies" or "associates" and companies in which Shell has joint control are referred to as "jointly controlled entities". In this presentation, associates and jointly controlled entities are also referred to as "equity-accounted investments". The term "Shell interest" is used for convenience to indicate the direct and/or indirect ownership interest held by Shell in a venture, partnership or company, after exclusion of all third-party interest.

This presentation contains forward-looking statements concerning the financial condition, results of operations and businesses of Royal Dutch Shell. All statements other than statements of historical fact are, or may be deemed to be, forward-looking statements. Forward-looking statements are statements of future expectations that are based on management's current expectations and assumptions and involve known and unknown risks and uncertainties that could cause actual results, performance or events to differ materially from those expressed or implied in these statements. Forward-looking statements include, among other things, statements concerning the potential exposure of Royal Dutch Shell to market risks and statements expressing management's expectations, beliefs, estimates, forecasts, projections and assumptions. These forward-looking statements are identified by their use of terms and phrases such as ''anticipate'', ''believe'', ''could'', ''estimate'', ''expect'', ''intend'', ''may'', ''plan'', ''objectives'', ''outlook'', ''probably'', ''project'', ''will'', ''seek'', ''target'', ''risks'', ''goals'', ''should'' and similar terms and phrases. There are a number of factors that could affect the future operations of Royal Dutch Shell and could cause those results to differ materially from those expressed in the forward-looking statements included in this presentation, including (without limitation): (a) price fluctuations in crude oil and natural gas; (b) changes in demand for Shell's products; (c) currency fluctuations; (d) drilling and production results; (e) reserves estimates; (f) loss of market share and industry competition; (g) environmental and physical risks; (h) risks associated with the identification of suitable potential acquisition properties and targets, and successful negotiation and completion of such transactions; (i) the risk of doing business in developing countries and countries subject to international sanctions; (j) legislative, fiscal and regulatory developments including potential litigation and regulatory measures as a result of climate changes; (k) economic and financial market conditions in various countries and regions; (l) political risks, including the risks of expropriation and renegotiation of the terms of contracts with governmental entities, delays or advancements in the approval of projects and delays in the reimbursement for shared costs; and (m) changes in trading conditions. All forward-looking statements contained in this presentation are expressly qualified in their entirety by the cautionary statements contained or referred to in this section. Readers should not place undue reliance on forward-looking statements. Additional factors that may affect future results are contained in Royal Dutch Shell's 20-F for the year ended 31 December, 2014 (available at www.shell.com/investor and www.sec.gov). These factors also should be considered by the reader. Each forward-looking statement speaks only as of the date of this presentation 2nd November 2015. Neither Royal Dutch Shell nor any of its subsidiaries undertake any obligation to publicly update or revise any forward-looking statement as a result of new information, future events or other information. In light of these risks, results could differ materially from those stated, implied or inferred from the forward-looking statements contained in this presentation. There can be no assurance that dividend payments will match or exceed those set out in this presentation in the future, or that they will be made at all.

We use certain terms in this presentation, such as discovery potential, that the United States Securities and Exchange Commission (SEC) guidelines strictly prohibit us from including in filings with the SEC. U.S. Investors are urged to consider closely the disclosure in our Form 20-F, File No 1-32575, available on the SEC website www.sec.gov. You can also obtain this form from the SEC by calling 1-800-SEC-0330.

Contents

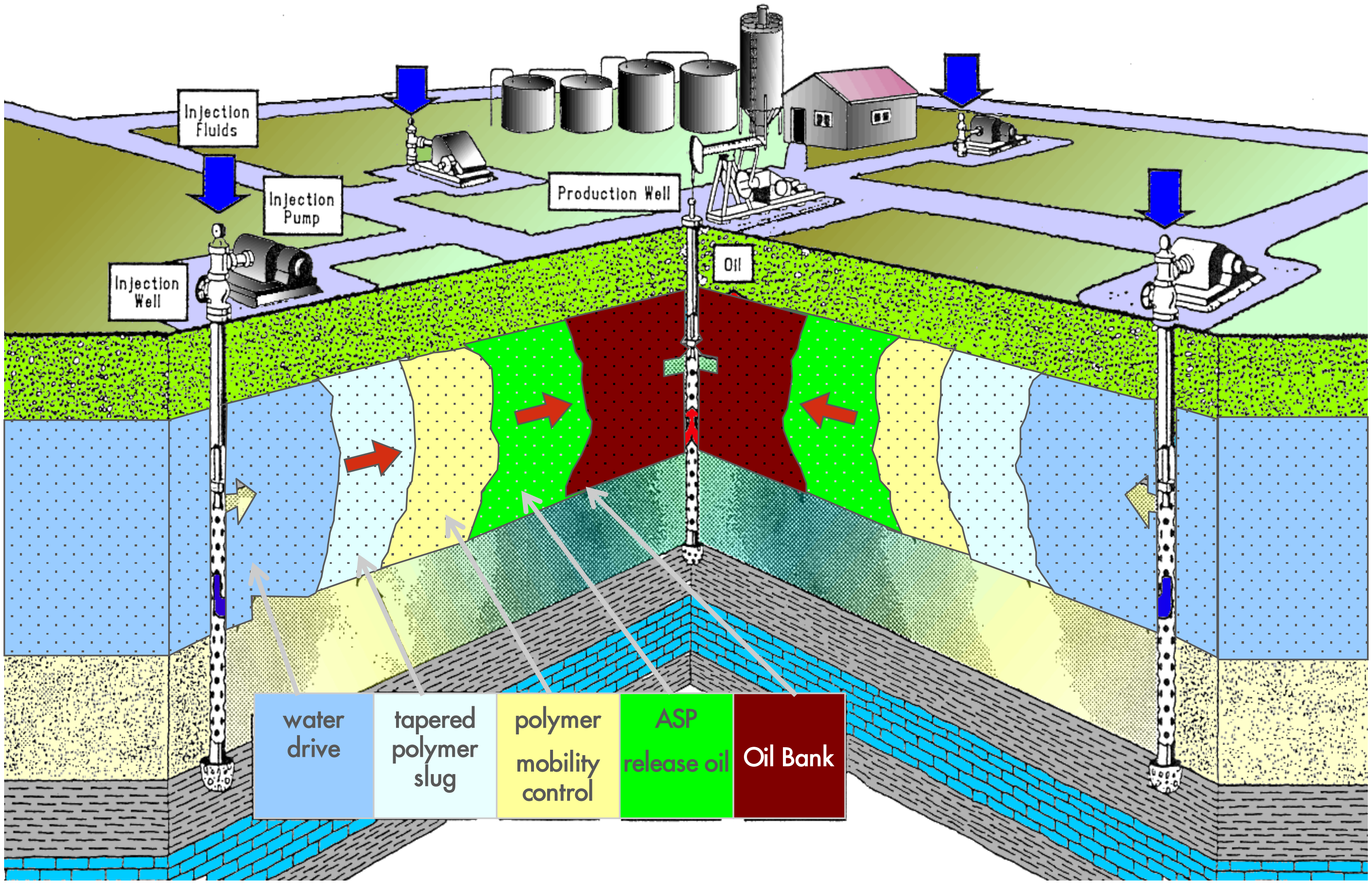
1. Surfactant chemistry and the sub-surface:
   - Why surfactants for Enhanced Oil Recovery (EOR)?
   - How they are matched to the reservoir
2. Upscaling surfactants for multi-well pilot
   - QA/QC to achieve product consistency and performance
   - Physical properties for handling and mixing
3. Conclusions

1.0

CHEMISTRY OF SURFACTANTS:

MATCHING TO THE SUB-SURFACE

ASP (Alkali, Surfactant, Polymer) flooding process

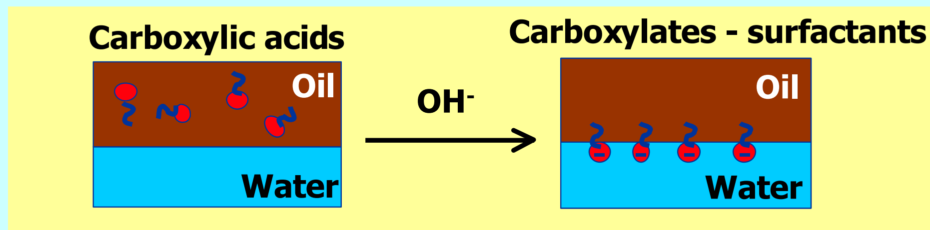


ASP: Alkaline Surfactant Polymer

Goal: Mobilise trapped oil, left behind after water flooding

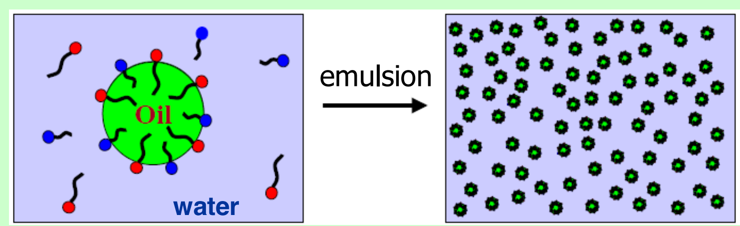
Alkali

- pH ~ 10-11
- natural surfactants (soaps)
- minimise surf. adsorption



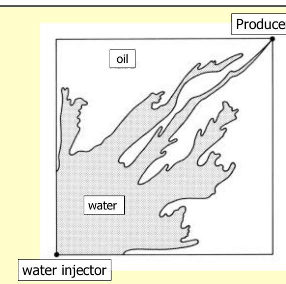
Surfactant

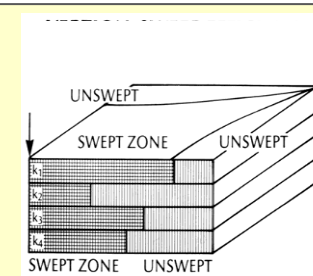
- lower IFT
- mobilise <u>residual</u> oil.



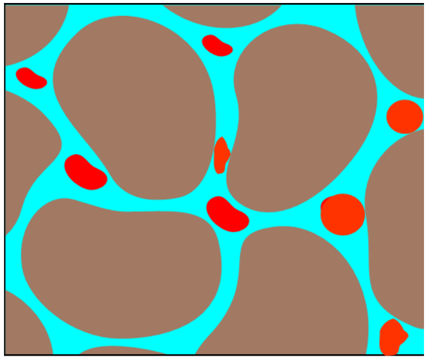
Polymer:

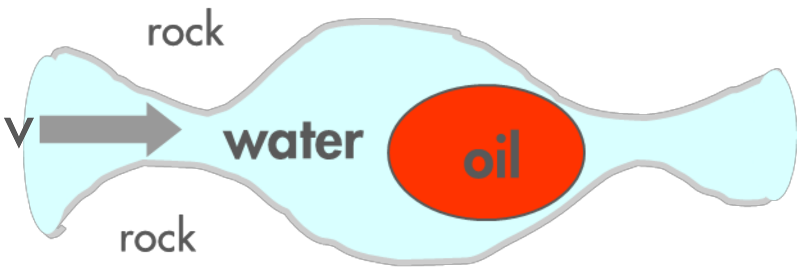
- increase viscosity
- improve mobility control

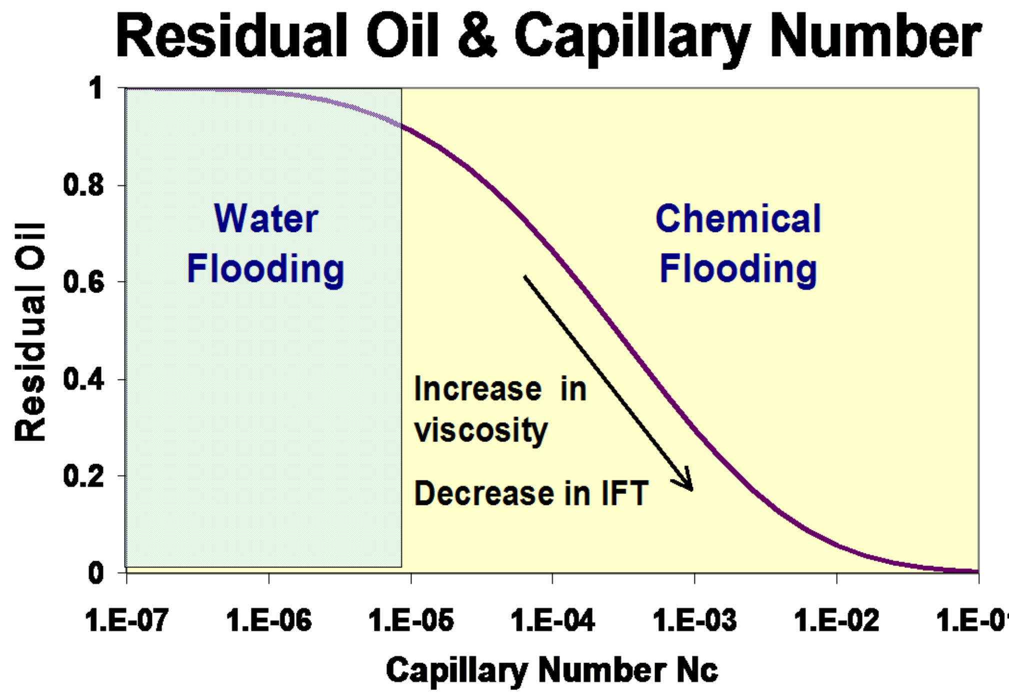




Why use surfactants for EOR?... Reduce residual oil saturation







PROBLEM

During water flooding, residual oil is trapped due to:

- low water viscosity (μ)
- high water-oil interfacial tension (σ)

SOLUTION

Increase capillary number Nc

$$N_c = \frac{\mu v}{\sigma}$$

- add viscosifying *polymer* ($\mu\uparrow$)
- add *surfactant* ($\sigma\downarrow$)

Desired surfactant properties for EOR

- Ultra-low IFT at low surfactant concentration (match to crude oil)
- Low emulsion viscosity, no liquid crystals
- Good aqueous solubility – clear solution
- Stable at reservoir temperature
- Low rock adsorption ➔ anionic surfactants
- Cost effective; available in large volumes

Microemulsion phase test or "salinity scan"

References: Many within Society of Petroleum Engineers (SPE).
e.g. SPE.115386. Recent Advances in Surfactant EOR. G.J. Hirasaki, et al

Surfactant types for chemical EOR

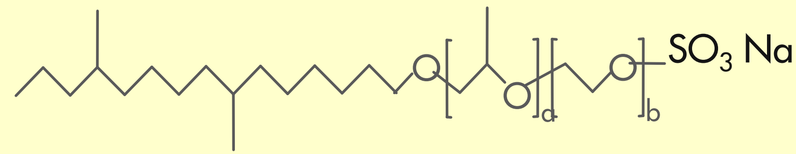
Most used surfactant families:

- Branched alcohol PO/EO sulfates
- Branched or twin-tailed sulfonates
- Binary blends

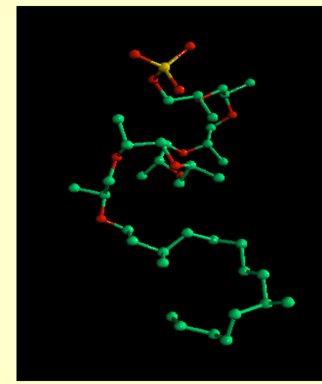
J000 branched $C_{12,13}$ alcohol developed for EOR (for AAS). Structure also has utility as (among others):

- Plasticizer alcohol
- Surfactant end-uses
- Synthetic lubricants, lubricant additives

Alcohol Alkoxy Sulfate (AAS) surfactants

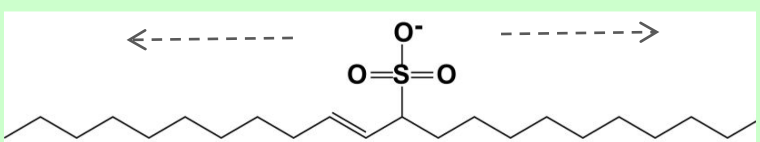


Shell ENORDET
A, J Series

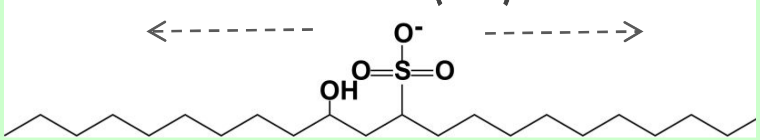


Sulfonate surfactants

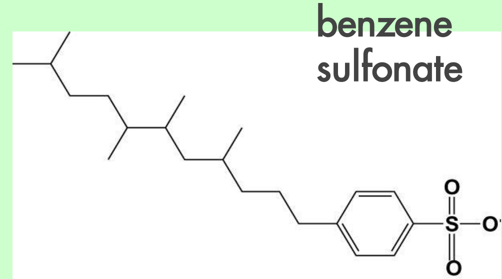
Shell ENORDET O Series



Internal olefin sulfonates (IOS)



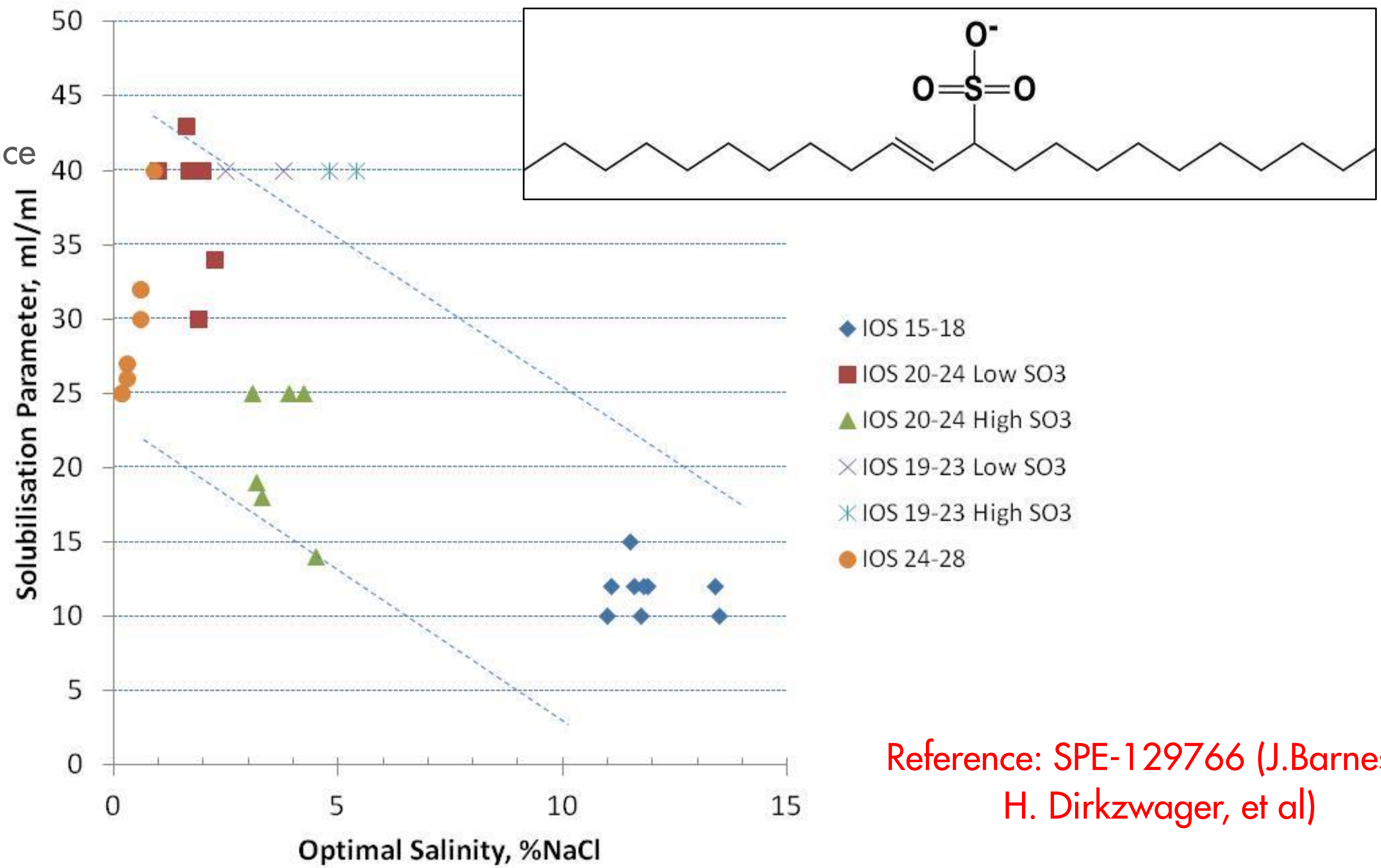
Branched alkyl benzene sulfonate



IOS surfactants – Tuning optimum salinity and IFT

Internal Olefin Sulfonates (IOS)

Lower IFT, better performance



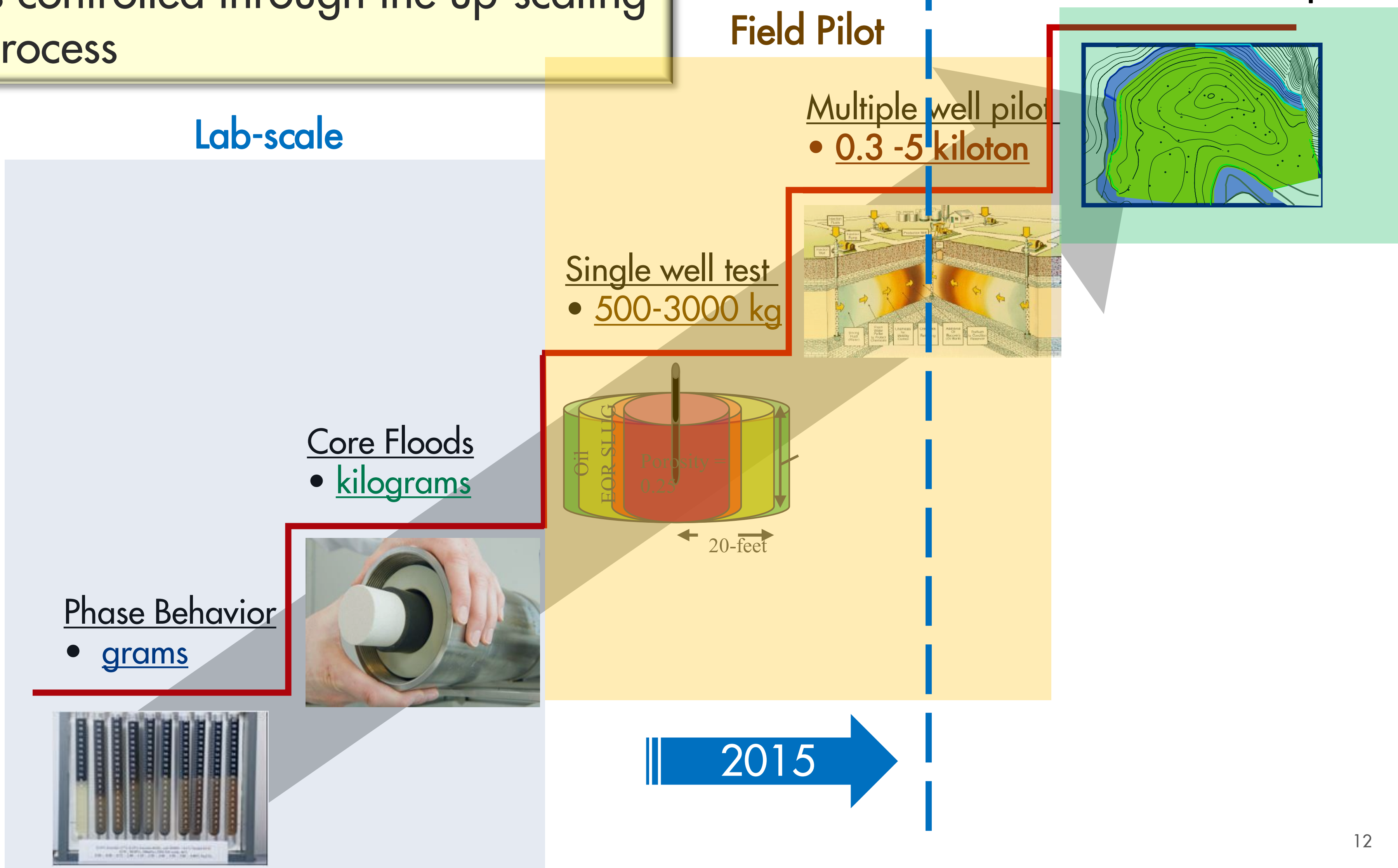
Reference: SPE-129766 (J.Barnes, H. Dirkzwager, et al)

2.0

UPSCALING AND QUALITY CONTROL OF SURFACTANTS

Surfactant up-scaling for EOR

Key requirement: surfactant quality is controlled through the up-scaling process



Surfactant project stages for a multi-well ASP (or SP) pilot

Team involved

Shell Chemicals

Customer / Operator

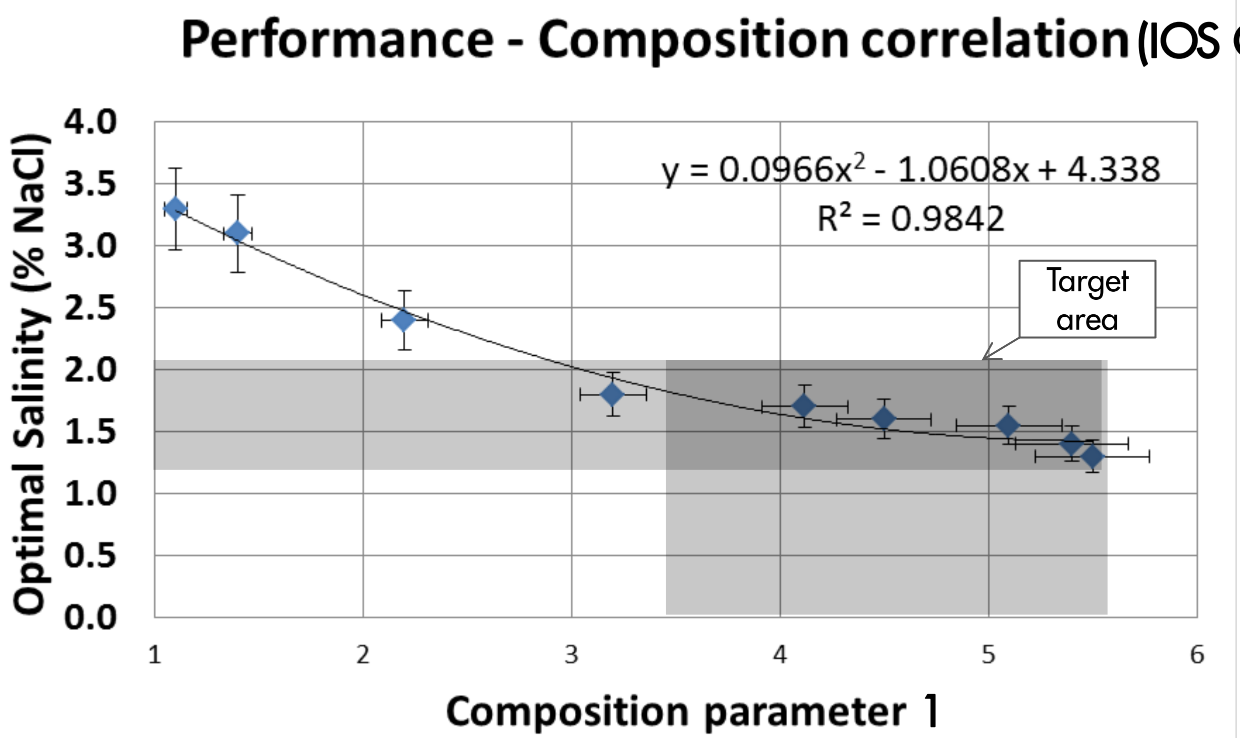
- Stage I: Feedstock production ✓
- Stage II: Pre-large scale production of surfactant(s) ✓
- Stage III: Large-scale production of surfactant(s) ✓
- Stage IV: Sub-surface (lab) performance check ✓
- Stage V: QA/QC of product at injection facilities ✓
- Stage VI: QA/QC of ASP injection fluid at injection facilities ✓

Recommended surfactant properties to assure surfactant quality

Property	What it relates to	Min.	Max.
Active matter content (wt%)	Chemical composition	x	y
Sodium sulphate (wt% on 100% AM)	Chemical composition	x	y
Residual sodium hydroxide (wt% on 100% AM)	Chemical composition	x	y
Unconverted feedstock (wt% on 100% AM)	Chemical composition	x	y
Carbon number distribution of hydrophobe	Chemical composition	x	y
Detailed analysis of sulfonated/ sulfated species	Chemical composition	x	y
Storage stability / shelf life at ambient temp (weeks)	Facilities: handling properties	x	y
Rheology in the appropriate temp range (cP)	Facilities: handling properties	x	y
Aqueous solubility at a particulat temperature	Sub-surface performance	x	y
Optimum salinity by phase behaviour (wt% NaCl)	Sub-surface performance	x	y
Solubilisation parameter (inversely related to IFT)	Sub-surface performance	x	y

Surfactants properties relate either to composition, handling or sub-surface performance

Stage II: Set manufacturing specs to target sub-surface performance (and physical stability)



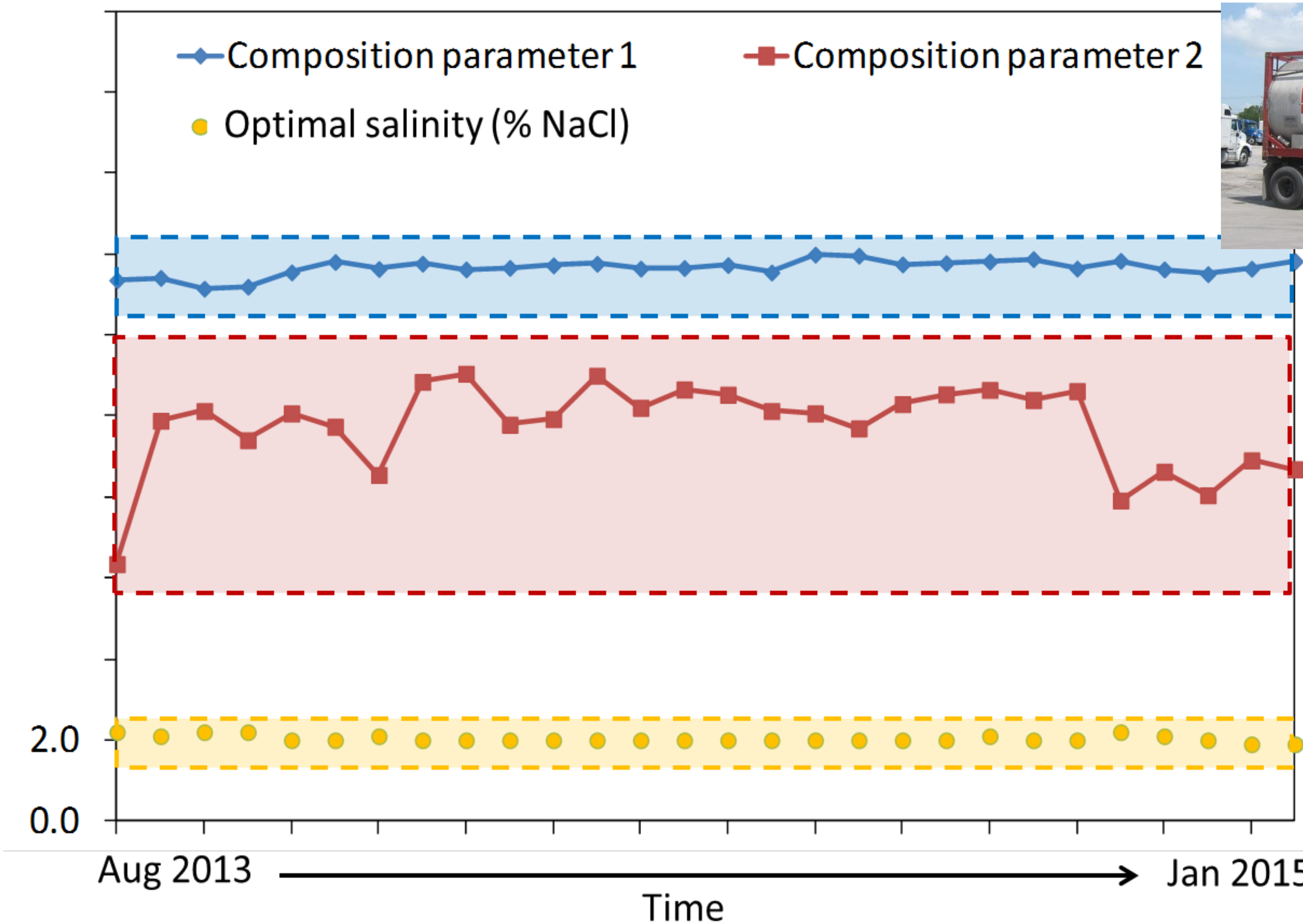
Sub-surface performance

Samples made with different equipment and process settings

Physical stability

Stage III: Case #1. Monitoring surfactant large-scale production

Internal olefin sulfonate C20-24 for ASP Multi-well pilot; ~6,000 tons surfactant



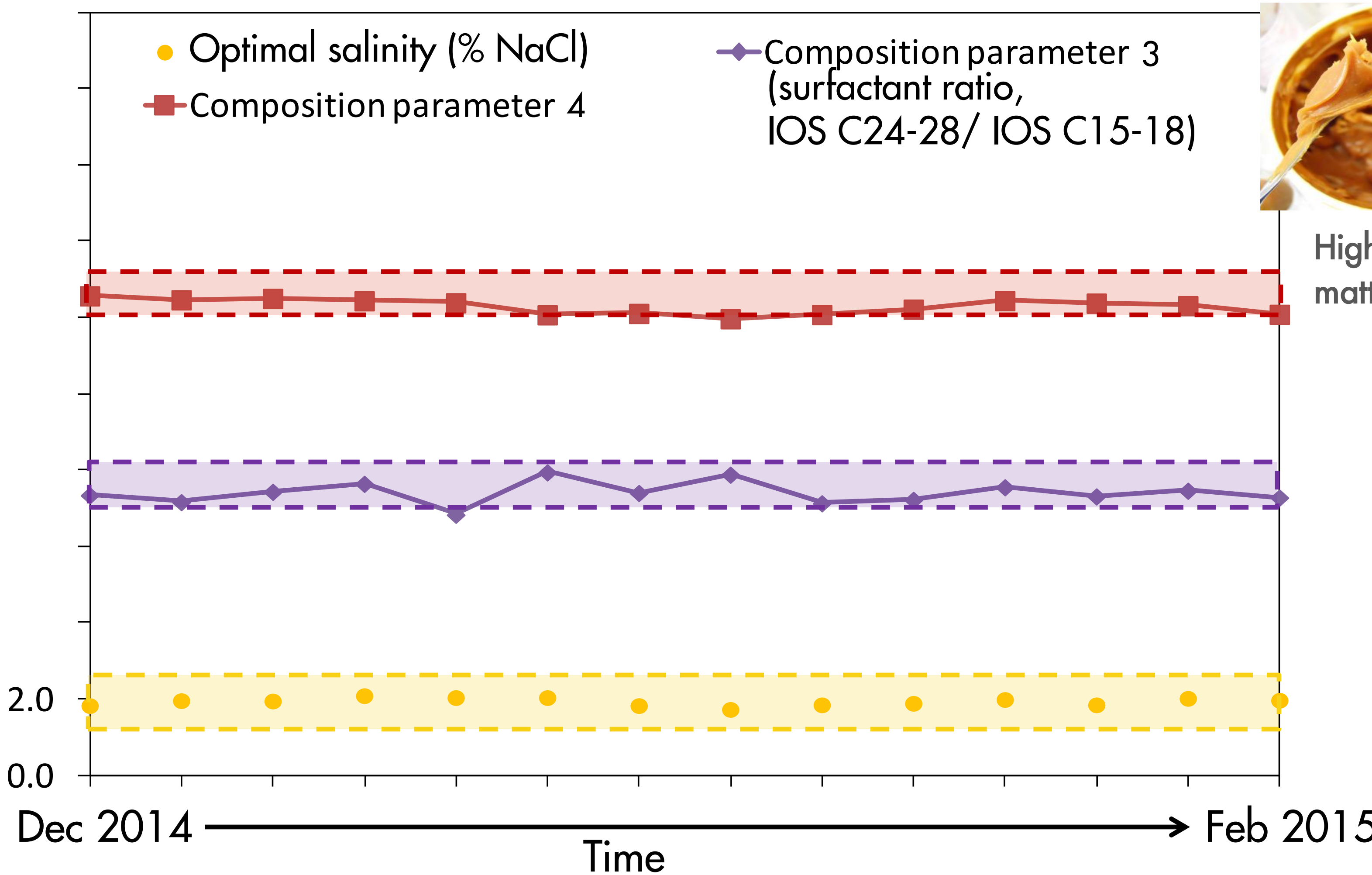
Lower active matter surfactant

Compositional data have been blinded

Colored boxes show target limits

Stage III: Case #2. Monitoring surfactant large-scale production

Internal olefin sulfonate blend for ASP Multi-well pilot; ~ 800 tons surfactant

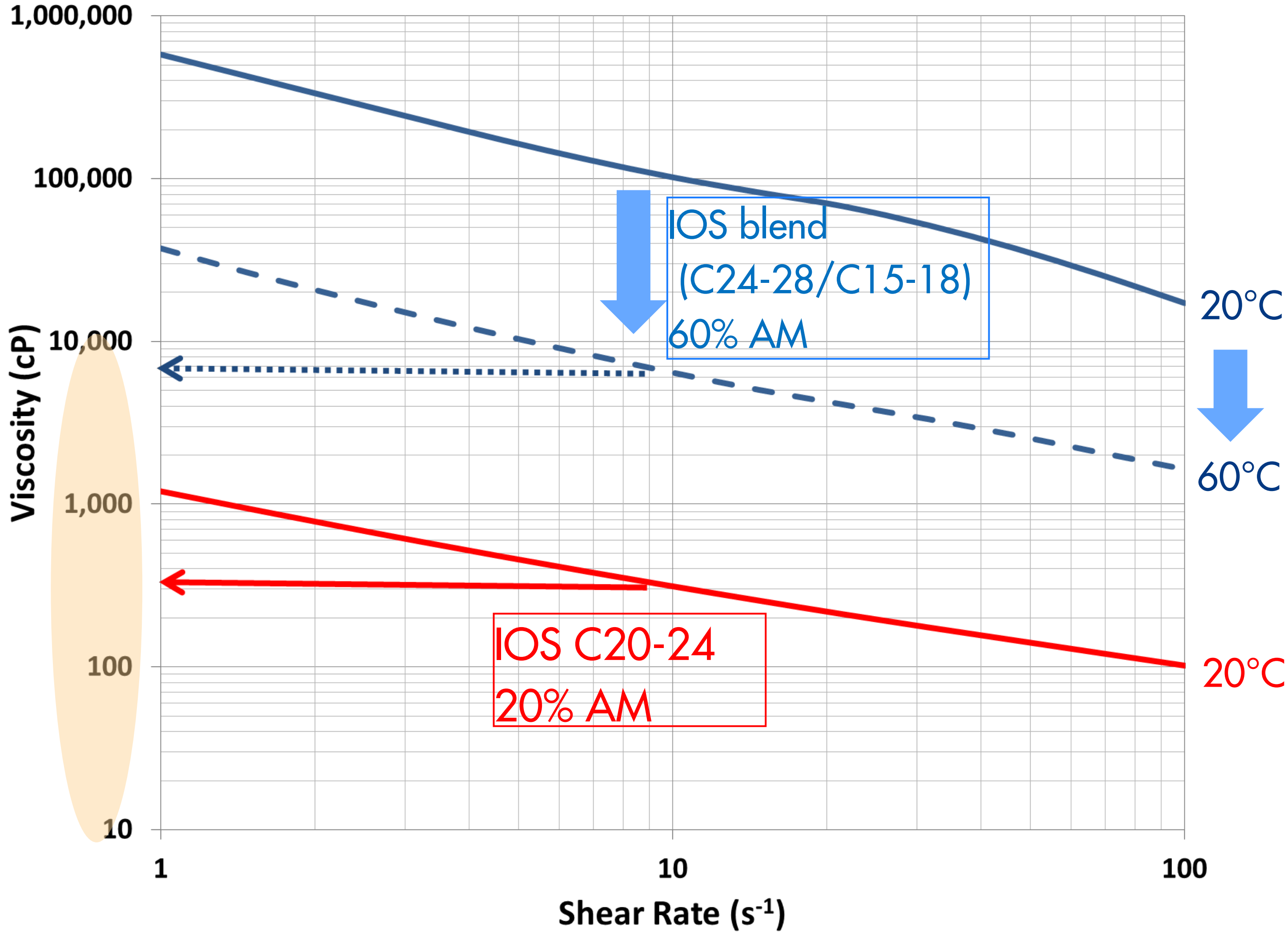


Higher active matter surfactant

Compositional data have been blinded

Colored boxes show target limits

Case #2: Higher active matter (60%) IOS is pumpable at 60°C



Viscosity of 60% AM IOS blend at 60°C is 6000 cP at 10s^{-1} shear rate, therefore pumpable. The 20% AM IOS is easily pumpable at 20°C.

Case #2: Handling high active matter IOS surfactant

Manufactured and pumped (hot) into 200 kg drums

Paste pumped out and mixed with water at pilot facilities

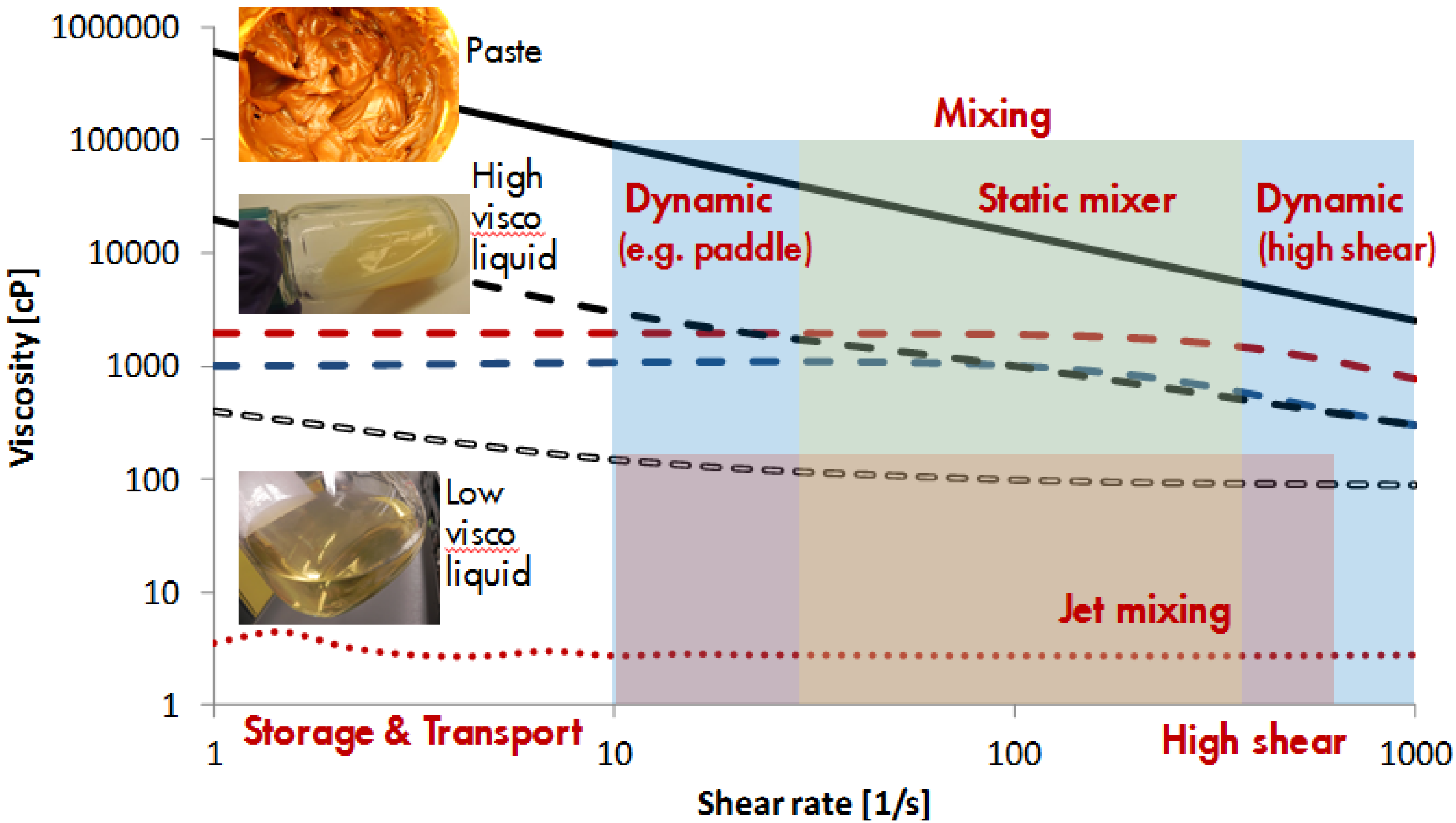
1. Drum pump extrudes paste

2. Paste mixed intimately with water

water

Injection well

Mixing method depends on surfactant concentrate properties



Conclusions, from a Surfactant Supplier perspective…

1. Initial laboratory phase: Match surfactants to reservoir (temperature, crude and brine)
2. Surfactant upscaling:
   a. Surfactant manufacturer and customer need to align (very large) surfactant volumes with surfactant manufacturing capability
   b. Good batch to batch consistency through:
      i. Documented QA/QC process, agreed early on in the project
      ii. Composition – performance correlations (for more emphasis on composition parameters)
   c. ~6,000 tons (low active matter) and ~800 tons (high active matter) surfactant produced for pilot trials
      i. Surfactant concentrate physical properties determine transport & mixing at facilities
3. Future: More handleable, high active matter to reduce shipping costs

Q & A