



6ª Jornada de
**Recuperación Mejorada
de Petróleo - EOR**
6 y 7 de noviembre - Mar del Plata



INSTITUTO ARGENTINO
DEL PETRÓLEO Y DEL GAS



7º CONGRESO IAPG
**Producción
y Desarrollo
de Reservas**

Thermal Stability Evaluation of EOR Polymers: Best Practices & Guidelines

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(SNF)





Introduction



Polymer flooding

- Proven technology worldwide
- Onshore and offshore



Current challenges

- Moving from PIT/pilot to full field
- Deployment in deeper reservoirs → temperature rising
- Looking @ offshore reservoirs → spacing & residence time ↗



Polymer stability in reservoir conditions = major concern

- Variations of protocols from lab to lab
- Bad protocols can lead to biased pessimistic results



Share 10+ years of lab experience and worldwide common practices



Layout

- Chemical degradation
- Thermal degradation
- Lab practices for thermal stability experiments

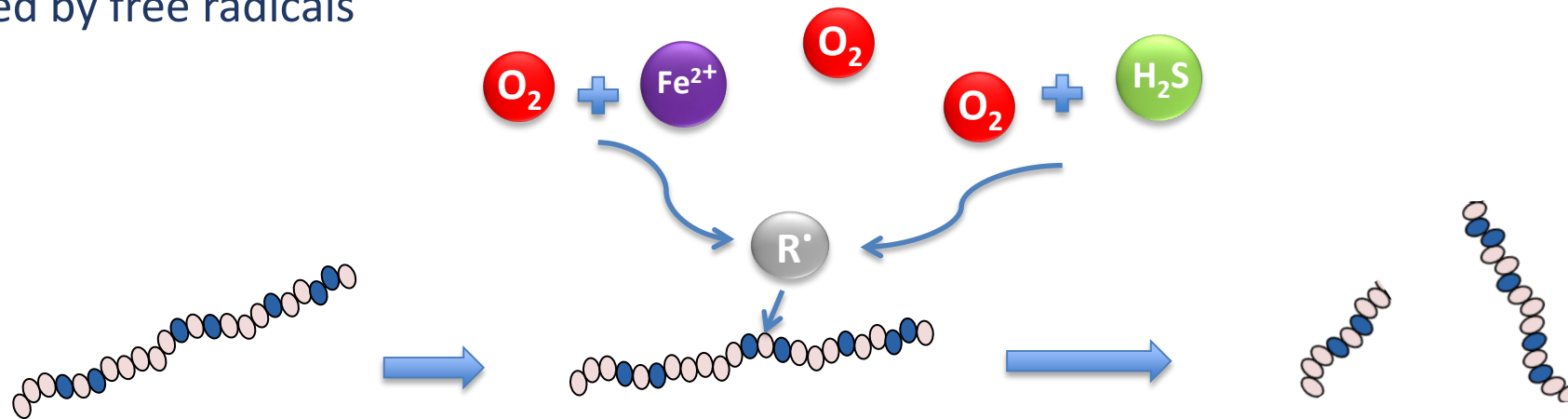




Chemical degradation

WHAT IS IT?

- Caused by free radicals



Red/Ox reactions

Viscosity +

$R^\bullet$ Free radical

Viscosity -



F3P polymers : Protected Polymer Package

Use of protective cocktails to minimize chemical degradation of polymers

Isopropanol / Thiourea / Water (ITW) – injected in Oman : huge amount of chemicals (300 ppm) cost + toxicity + flammability

Friendly additives can be added in polymer formulation

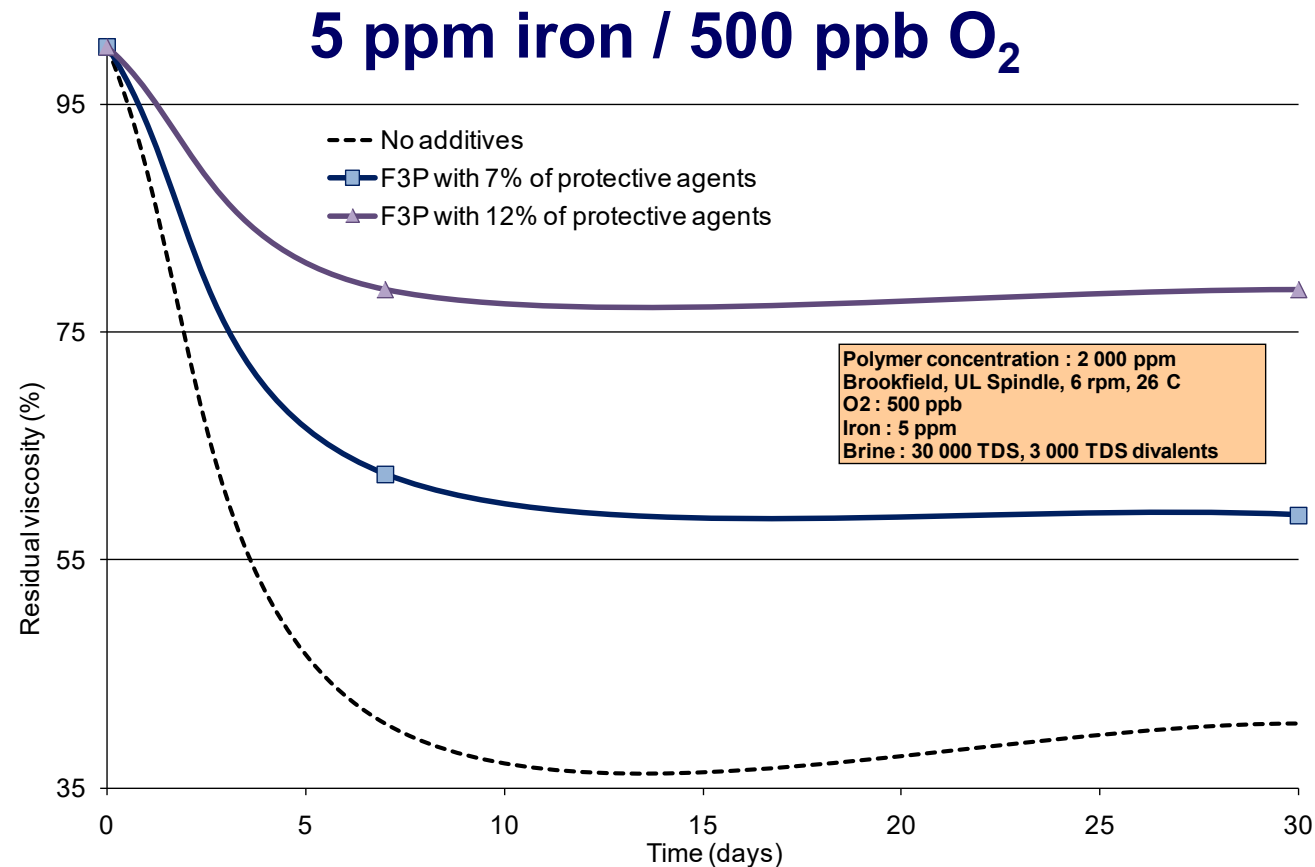
- Protective package added at the manufacturing stage
- Package tailored to field conditions
 - Iron content
 - H₂S content
 - O₂ content

SPE 129756 Patent WO 2010/133258





Impact of iron on stability



Integration of protective additives in the polymer formulation (F3P) significantly decreases polymer viscosity loss due to contaminant

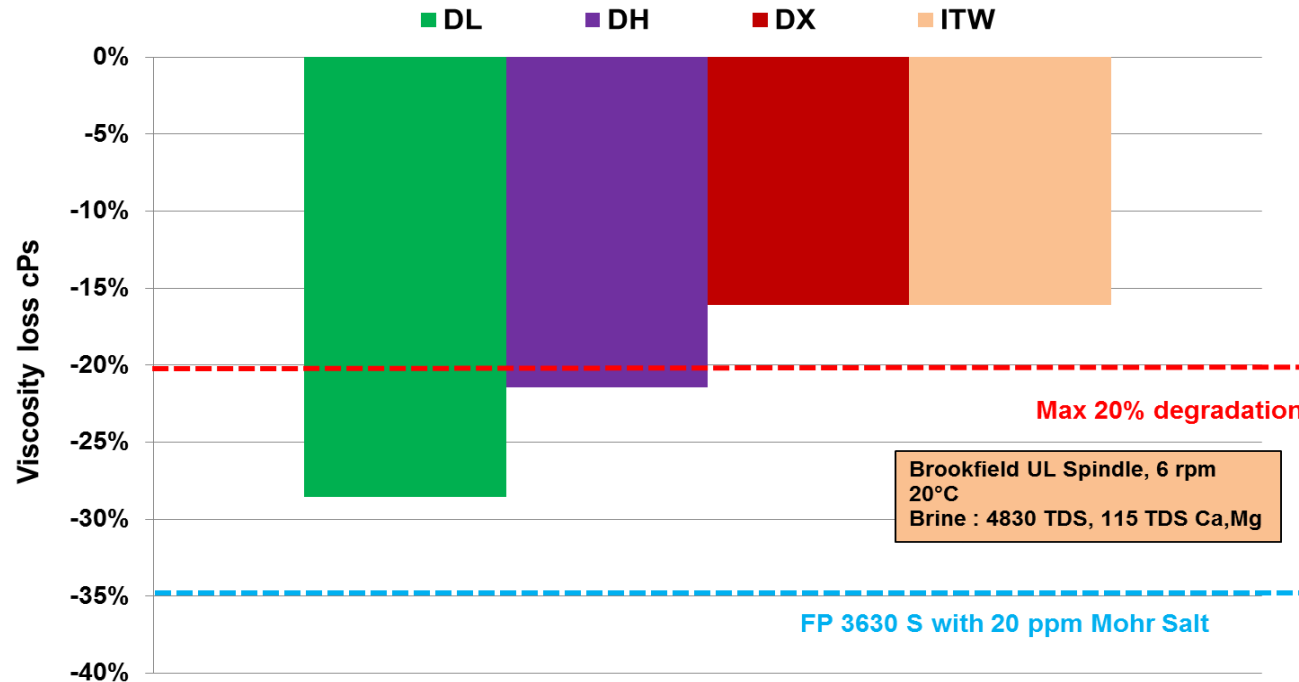


Fast Stability tests : Stability to Fe²⁺/O₂

Experiment = 20 minutes at air atmosphere : addition of 20 ppm of Mohr salt in a solution of polymer

FP 3630S (1000 ppm)

ITW = 10% thiourea+ 20% isopropanol



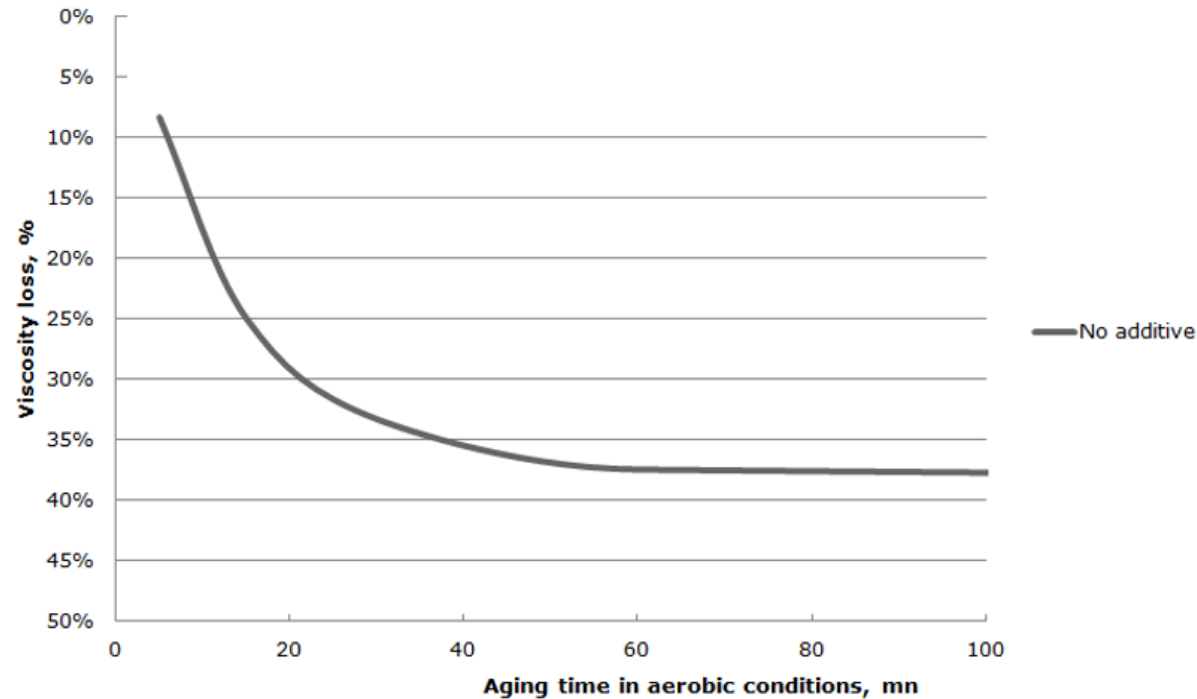
Non protected polymers → degradation = 35%

Fine-tuned protective package DX and ITW → less than 20% of degradation



Sampling on site : oxidative degradation

- 50 ppm of H₂S in injection water, no oxygen
- Sampling container filled to avoid any shear degradation and oxygen ingress
- Back to the lab : exposure to air atmosphere

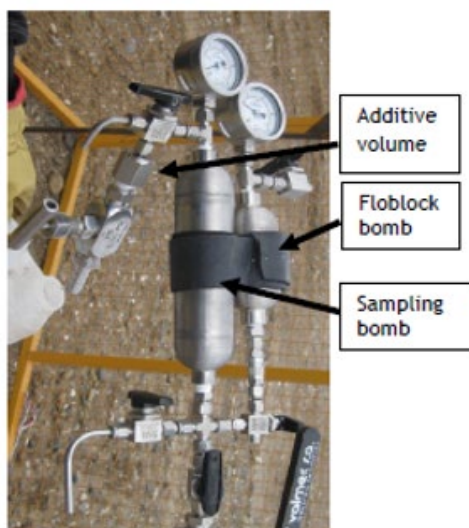




Sampling on site to avoid oxidative degradation

Addition of protective additives during sampling

Sampling unit in field conditions



Exposure to air

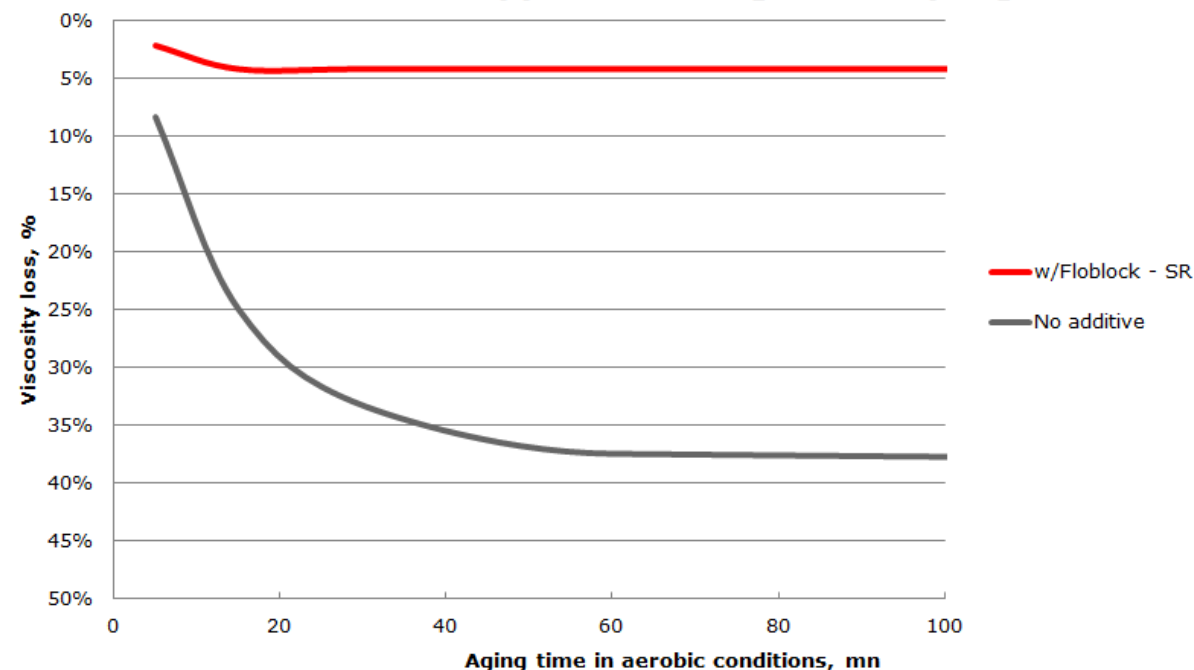


SPE 164121

Effective Propagation of HPAM Solutions through the Tambaredjo Reservoir during a Polymer Flood

R.N. Manichand, SPE, K.P. Moe Soe Let, SPE, Staatsolie Suriname, J. Kiefer, SPE, L.Gil, SPE, B.Quillien, SPE, SNF SAS, and R.S. Seright, SPE, New Mexico Tech

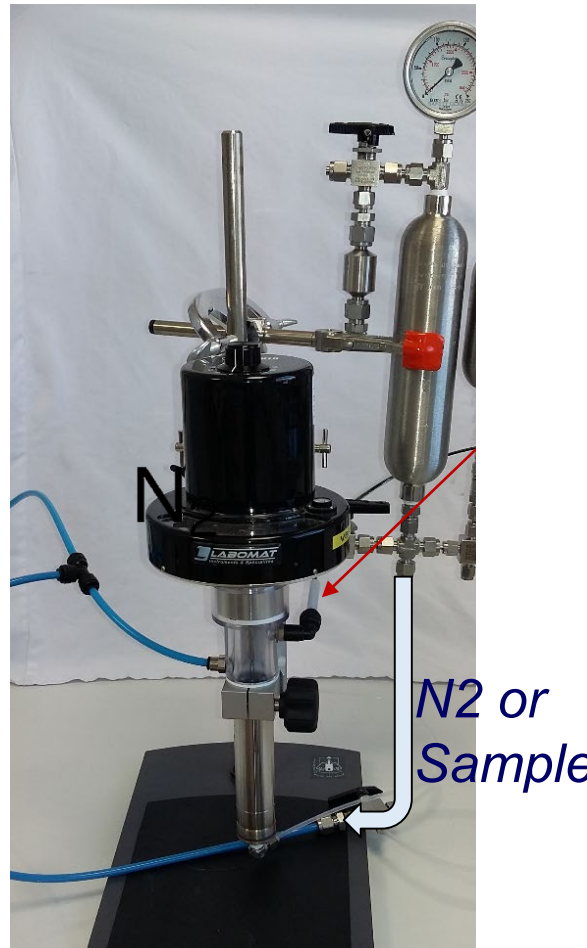
Effect of Floblock SR on polymer solution viscosity with 50 ppm H₂S using the sampling unit



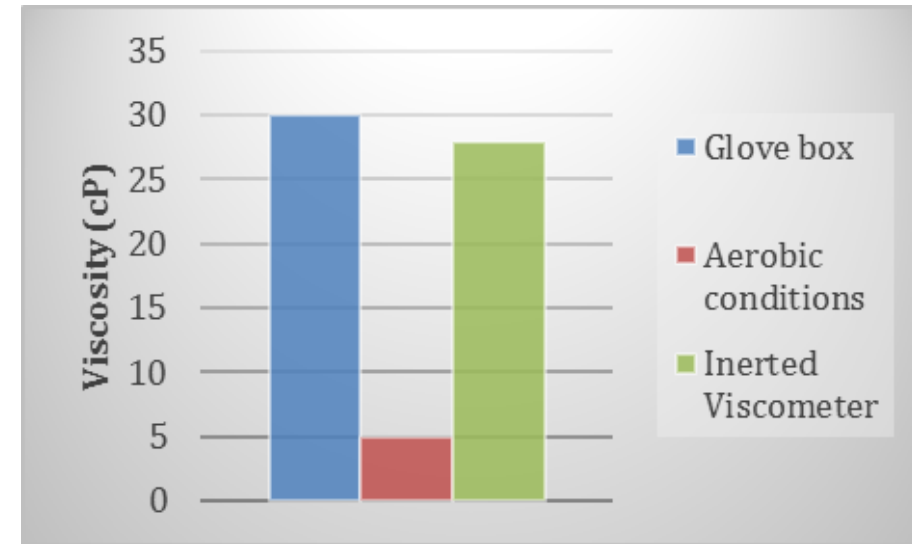
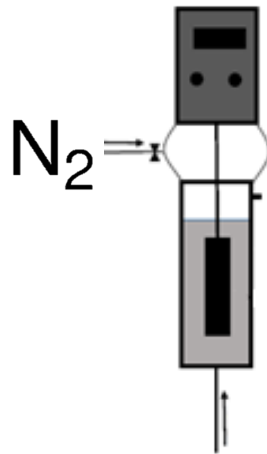


Sampling to avoid oxidative degradation : O₂F

Specific design to transfer the sample from the sampling container to the Brookfield cup under nitrogen



O₂ probe



Mitigation of oxidative degradation



Chemical degradation

- Chemical degradation occurs in presence of contaminants and especially **oxygen, iron, H₂S**
- Reaction between these contaminants => formation of free radicals => degradation of polymers
- Reducing polymer degradation encompasses:
 - Adapting injection strategy and auxiliary chemicals → **NO OXYGEN = NO PROBLEM**
 - Adapting chemistry and including protective additives → **F3P**
 - Sampling on site can lead to mis-leading results → **use of appropriate sampling and measuring tools**



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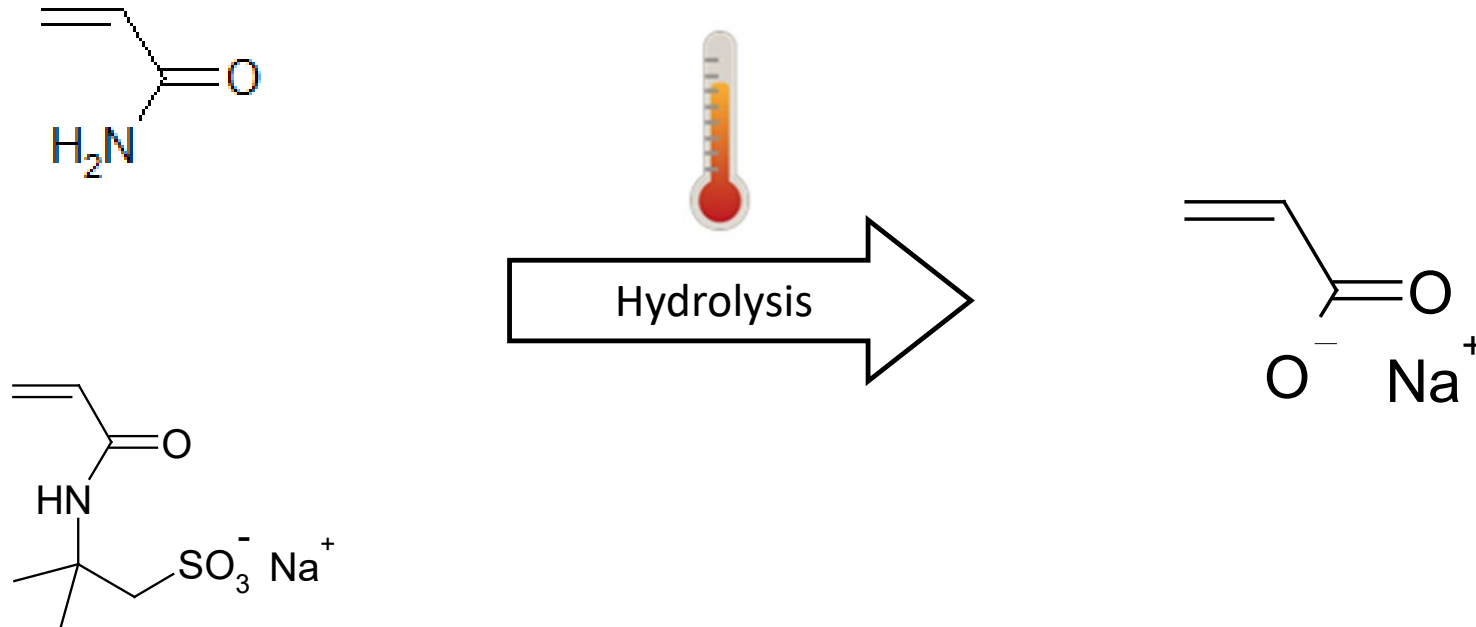
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Thermal degradation of polymers



Thermal degradation of polymers

- Mechanism

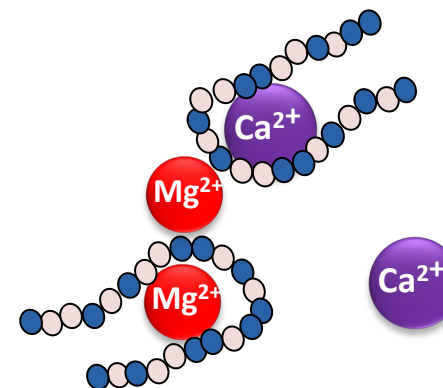
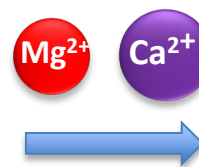
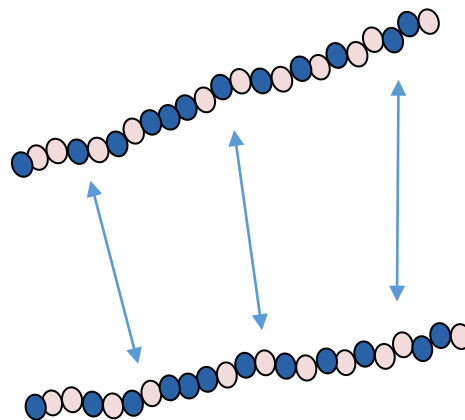
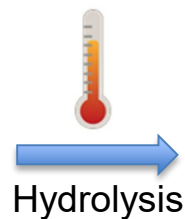
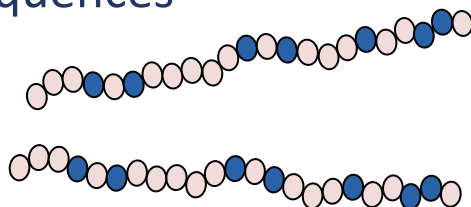




Introduction

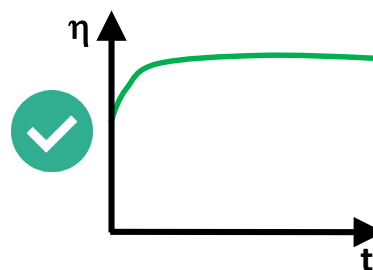
Thermal Degradation

- Consequences

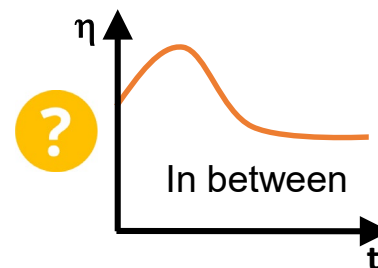
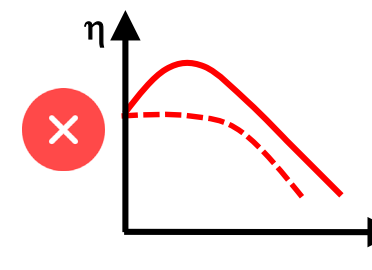


● Negative charge

no/low divalents



with divalents





How to Mitigate Degradation?



On the field

- Choose the right polymer
- N₂ blanketing
- O₂ scavenger
- Reservoir = strong reducer



In the lab

- Specific protocols are required

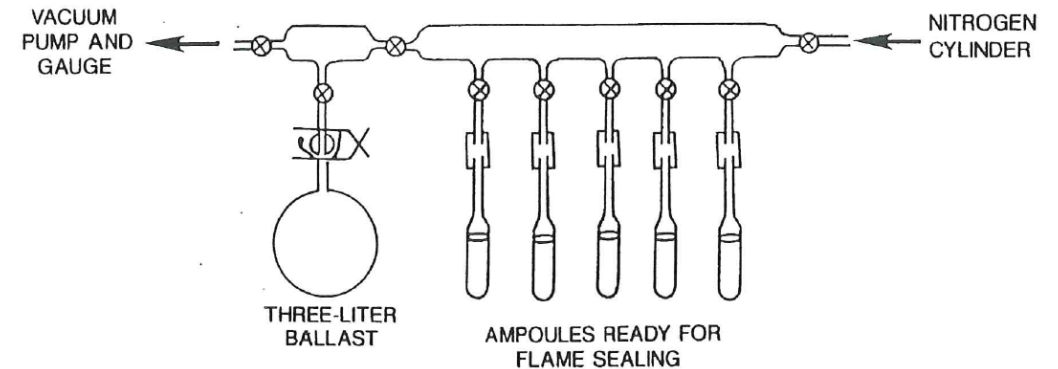
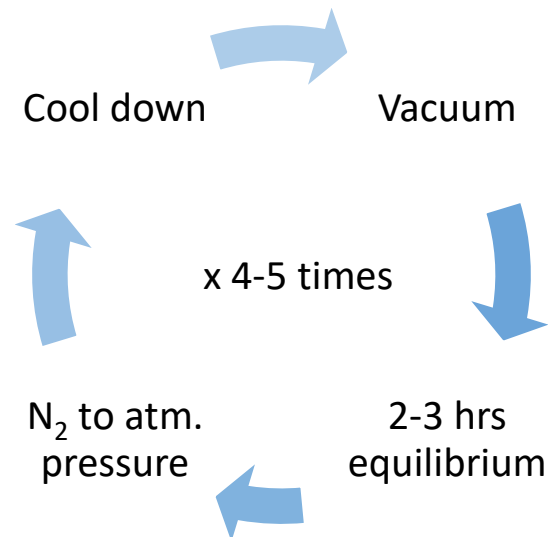
lab evaluation artefacts can kill projects



API Recommended Practice

Preparation of vacuum sealed glass ampoules

- Several cycles procedure rarely fully applied



- [O₂] $\leq \leq \approx 100$ ppb
- Risks and limitations



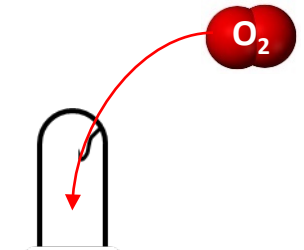
time consuming



cuts



burns



cracks (O₂ ingress)

(Levitt *et al.*, 2008, SPE 113845)



Preferred Glove Box Method

Advantages

- Ultra low dissolved $[O_2]$ ($\approx 5-15$ ppb)
- Time saving
- Only one cell/condition for the whole study



NMR characterization

(Sandengen *et al.*, 2017, Journal of Pet. Sci. Eng. 158 (2017) 680-692)



In-glovebox viscosity
measurment



Polymer Preparation

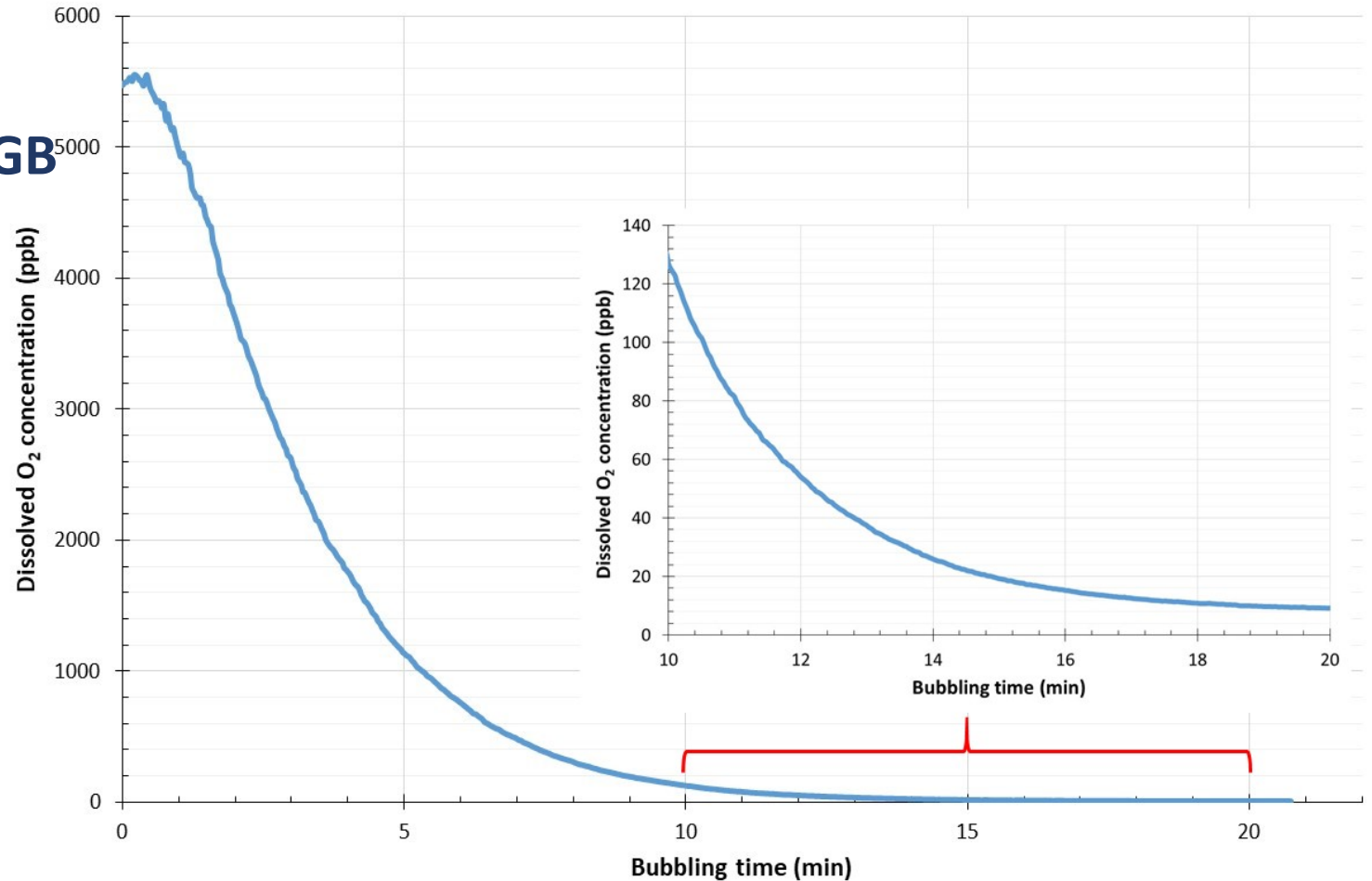
Option 1 = polymer preparation in GB

- Brine deoxygenation
- Dissolution & dilution of the polymer solution

1L brine sample

=

20 min bubbling time

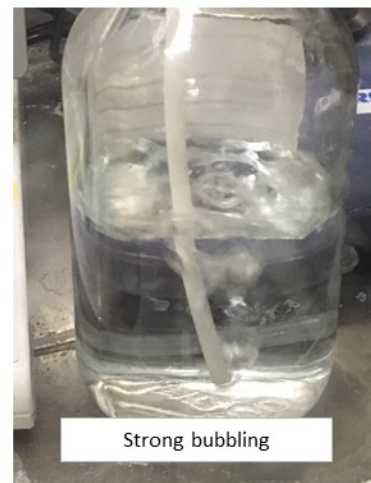
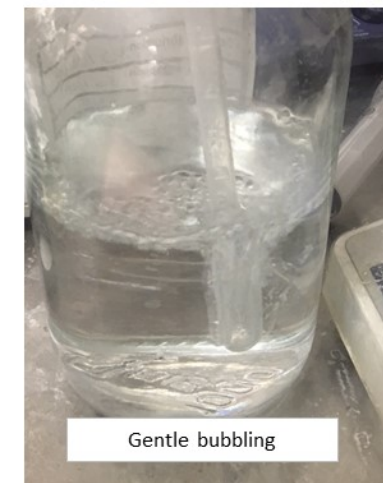
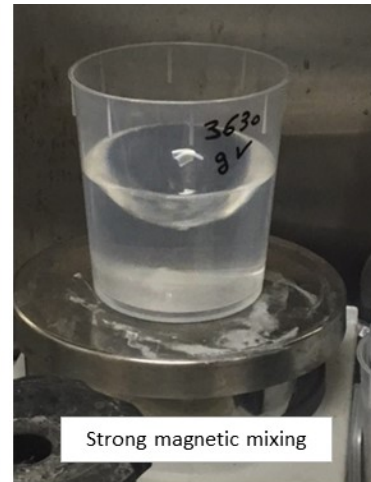
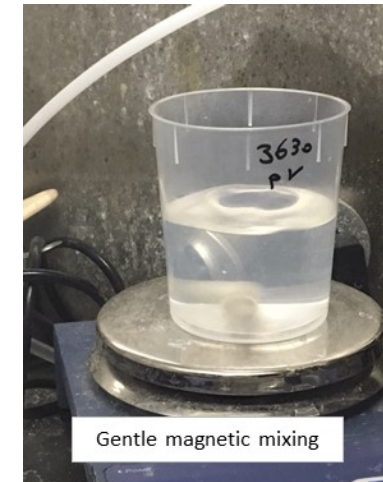
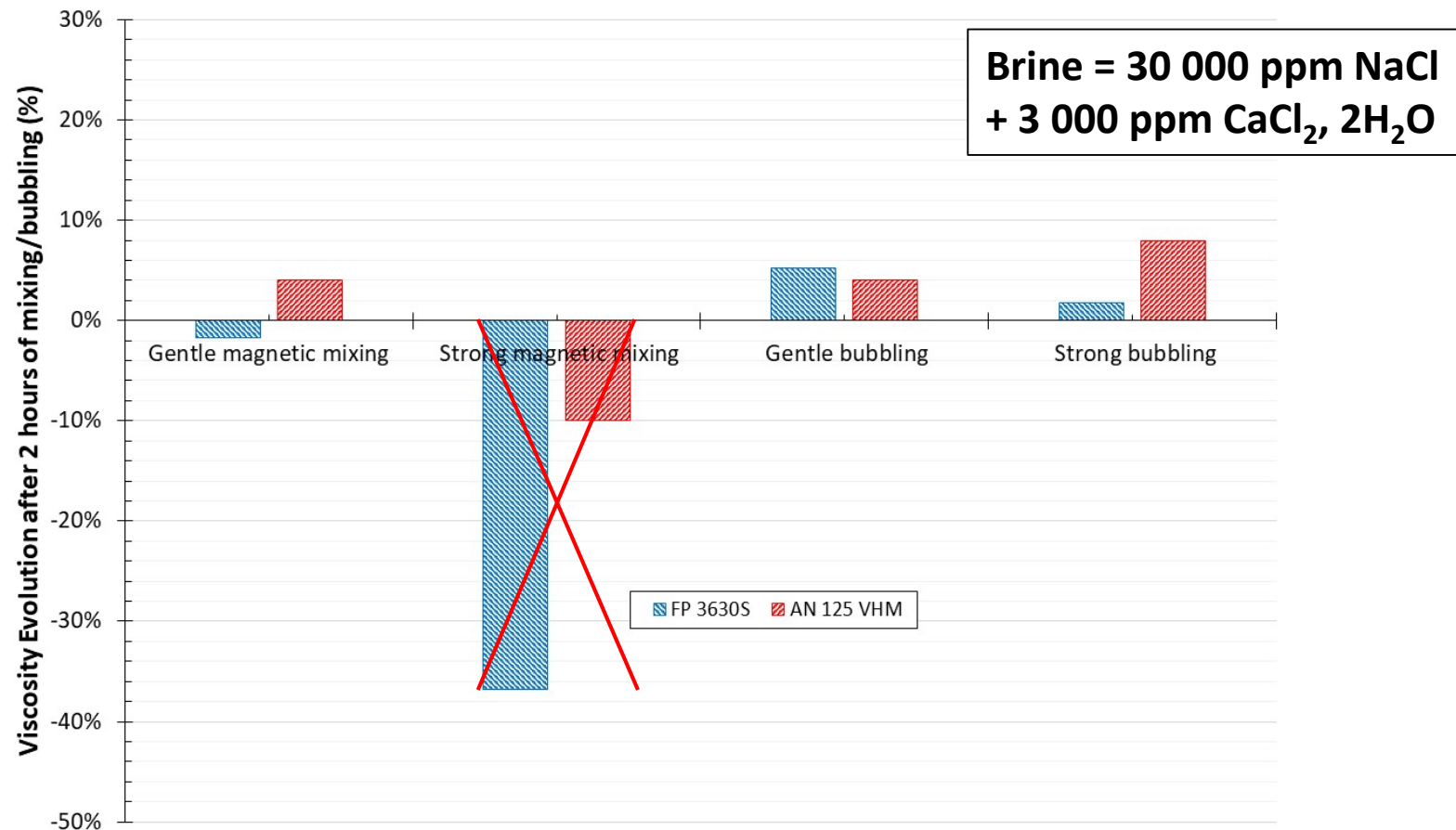




Polymer Preparation

Option 2 = polymer preparation outside GB followed by deoxygenation in GB

- Impact of deoxygenation method





Impact of Container Type

Ampoules / Bottles commonly found in the EOR labs





Impact of Container Type

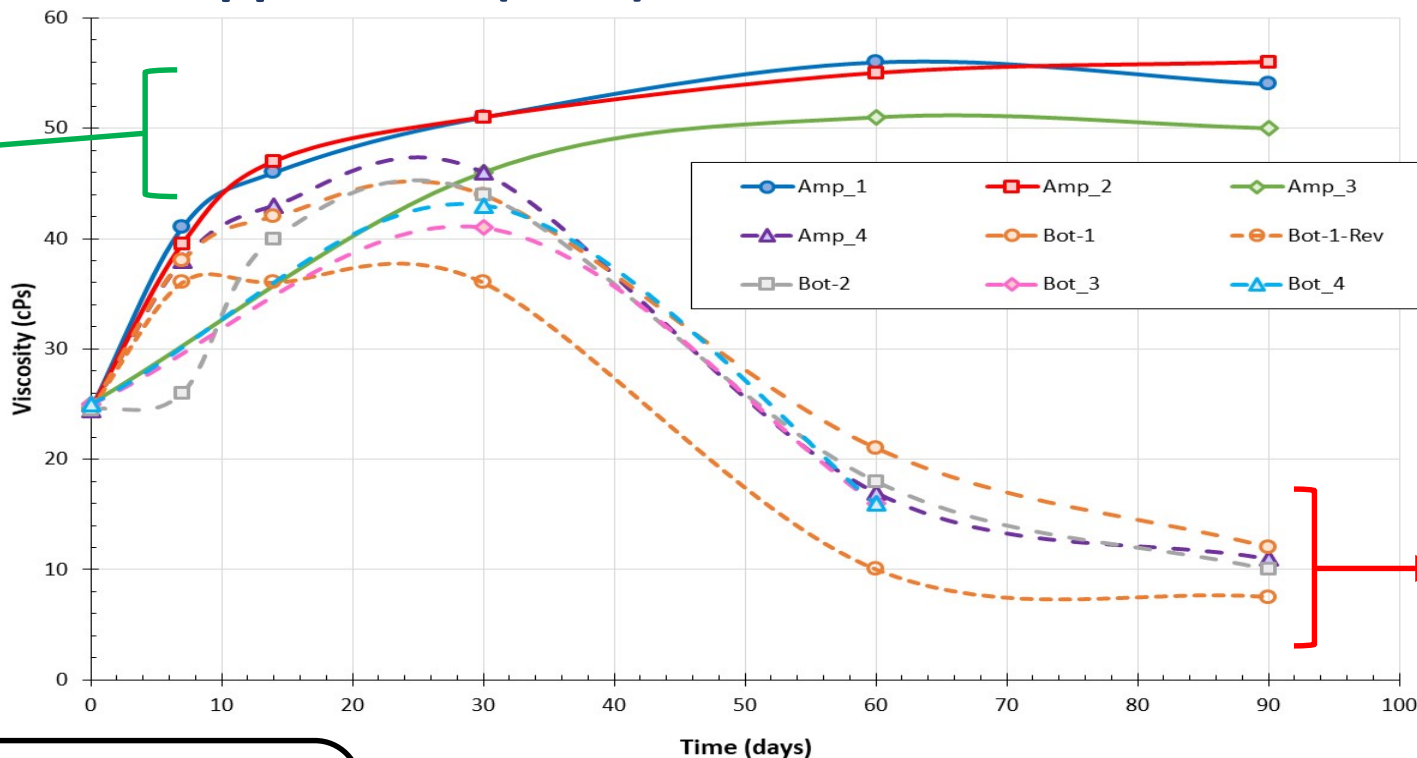
AN 105 VHM in 30 000 ppm NaCl (78°C)



Amp_1



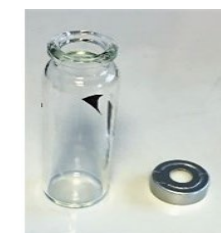
Amp_2



Amp_4



Bot_1



Bot_2, 3 & 4

Learnings

- Ensure sealing
- Avoid contact with seals or o-rings

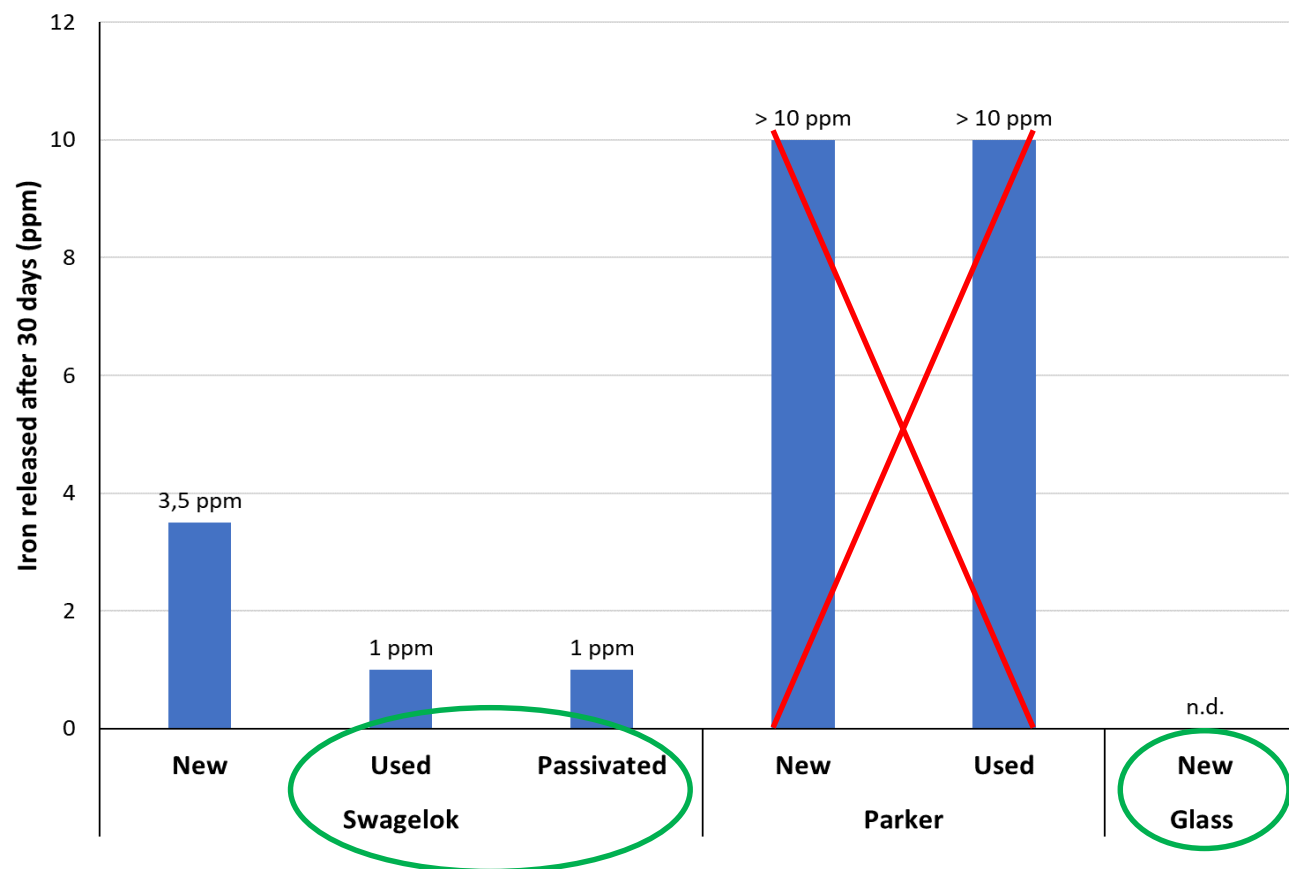


Leak suspected + contamination with radicals



Ampoules Provider Matters

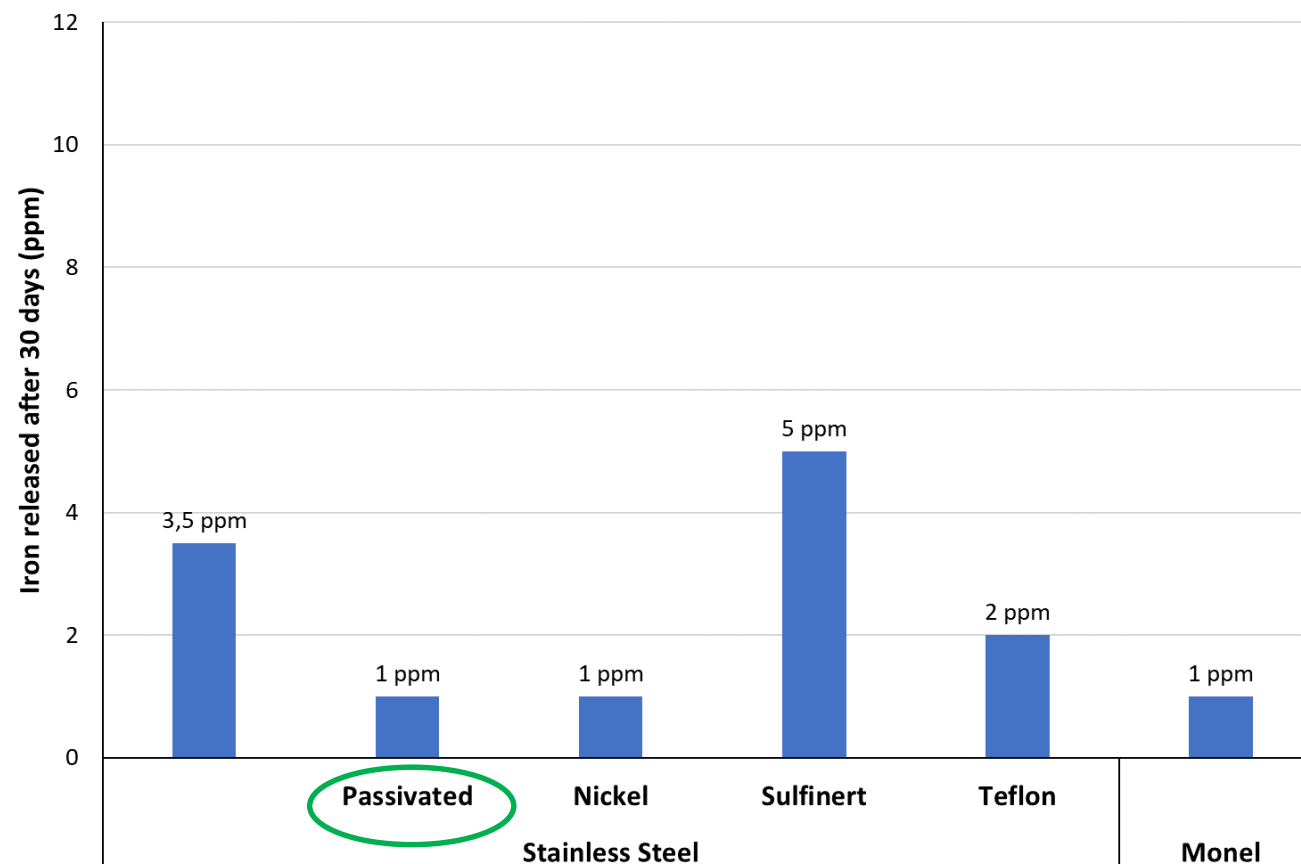
AN 105 VHM in 50 000 ppm NaCl (105°C)





Does Surface Treatment or Alloy Make It Better?

AN 105 VHM in 50 000 ppm NaCl (105°C)





Conclusions

Glove box = reliable, efficient ultra O₂ conc. ($\approx$ 5-15 ppb)

Polymer solution can be prepared either in/outside the glove box

- Be careful with stirring the polymer solution for deoxygenation
- Nitrogen bubbling is preferred

Choice of the container is key

- Main commercial ampoules/bottles are subject to leak during cooling/heating
 - Pessimistic stability results
- Homemade glass ampoule was developed with specific glass to glass sealing



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THANK YOU

Questions

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