Thermodynamic hydrate inhibitors.

Consequences for carbonate scale formation during oil and gas recovery in pH stabilized systems

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Outline of presentation

- **The importance of basic chemistry know how for the understanding of carbonate scale problems in the oil and gas industry**
- **What is pH stabilisation and where is it used?**
- **What is the influence on $CaCO_3$ scale formation of thermodynamic hydrate inhibitors?**
- **The Kollsnes gas export plant and the $NaHCO_3$ scale problem**

Types of inorganic scale

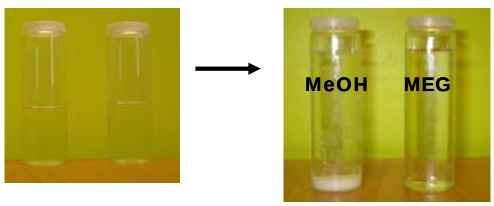
- Sulphates
  - Barite ($BaSO_4$)
  - Gypsum ($CaSO_4 \cdot 2H_2O$)
  - Anhydrite ($CaSO_4$)
  - Celestite ($SrSO_4$)
- Carbonates
  - $CaCO_3$, $BaCO_3$, $SrCO_3$, $MgCO_3$ and $FeCO_3$
  - $Na(K)HCO_3$, $Na(K)_2CO_3$
- "Exotic" scales
  - Silicates (Si…)
  - Halite (NaCl)

Not pH dependent (sulphates)

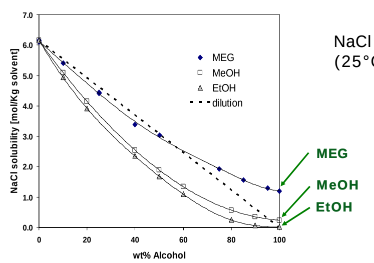
pH dependent (carbonates)
CO_2/H_2S distribution

Salting out

- **Start**:
  - Aqueous NaCl(sat) solution
- **Add alcohol to NaCl(sat) solution**:
  - NaCl(s) formed in MeOH
  - No "Salting Out" in MEG



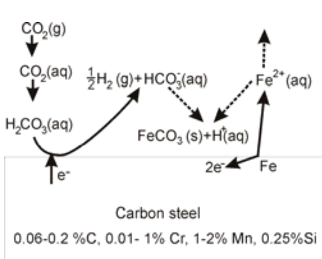
Salting out



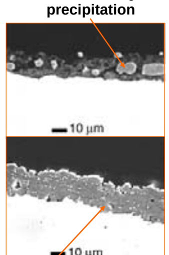
NaCl Solubility (25°C)

- **Severe "salting out" expected in solutions of water+MeOH and water+EtOH**

Corrosion protection - "pH Stabilization"

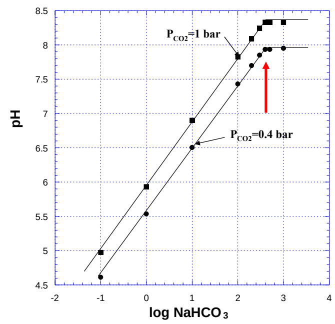


Initial $FeCO_3$ precipitation



Protective $FeCO_3$ film

Solubility of $NaHCO_3$ at 25ºC From MultiMEGScale



Solubility of $NaHCO_3$ in a 73wt% MEG - 27wt% water solution. The total pressure is similarly 1 and 0.4 bar, respectively.

260 mmole/kg solvent

The $NaHCO_3$ solubility increases with T and is at 73 wt% MEG
375 mmole/kg solvent at 25ºC and
697 mmole/kg solvent at 80ºC.

Why is alkalinity important?

- pH and carbonate scale potential is controlled mainly by
  - Alkalinity - most important
  - Organic acids - very important
  - CO_2 (and H_2S) pressure - very important
  - Ion concentrations in water - very important

Alkalinity

- Alkalinity should be defined such that it can be easily analyzed (titration) and used in calculations
- System: H_2O-$NaCl$-$CaSO_4$-CO_2-H_2S-HAc
- Electro neutrality:

$$m_{Na^+} + 2m_{Ca^{2+}} + m_{H^+} = m_{OH^-} + m_{Cl^-} + 2m_{SO_4^{2-}} + m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{HS^-} + m_{Ac^-}$$

- Rearrange to get pH independent on one side

$$\underbrace{m_{Na^+} + 2m_{Ca^{2+}} - m_{Cl^-} - 2m_{SO_4^{2-}}}_{\text{pH independent}} = \underbrace{m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{HS^-} + m_{Ac^-} + m_{OH^-} - m_{H^+}}_{\text{pH dependent}}$$

$$A_T = m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{HS^-} + m_{Ac^-} + m_{OH^-} - m_{H^+}$$

Changing alkalinity

Addition of:

- $NaCl$, $CaSO_4$: No effect
- HAc: No effect — $HAc \rightarrow H^+ + Ac^-$
- CO_2- pressure: No effect — $CO_2 + H_2O \rightarrow H^+ + HCO_3^-$; $CO_2 + H_2O \rightarrow 2H^+ + CO_3^{2-}$

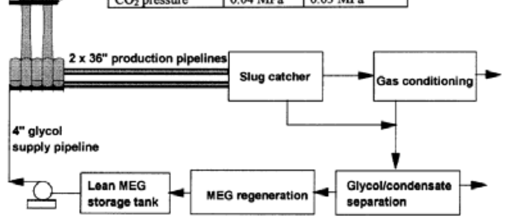
- $NaHCO_3$, NaAc, NaOH: Increase A_T factor 1
- $CaCO_3$: Increase A_T factor 2
- HCl: Decrease A_T factor 1

$$m_{Na^+} + 2m_{Ca^{2+}} - m_{Cl^-} - 2m_{SO_4^{2-}} = m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{HS^-} + m_{Ac^-} + m_{OH^-} - m_{H^+}$$

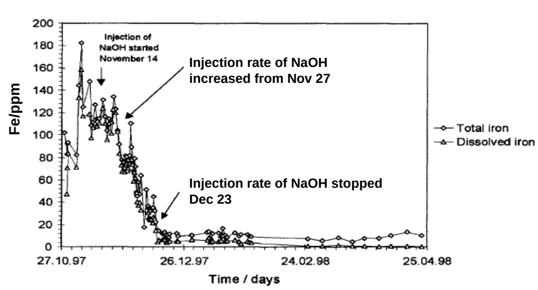
The Troll production system

Corrosion 99. A paper by S. Olsen, O Lunde Statoil and A. Dugstad IFE

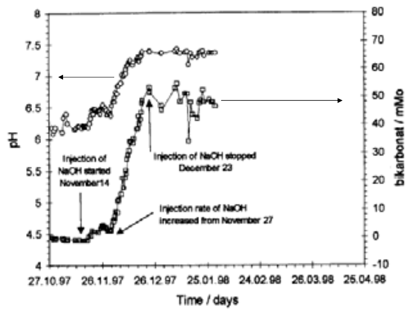
Parameter	Pipe inlet	Pipe outlet
Temperature	50 °C	5 °C
CO_2 pressure	0.04 MPa	0.03 MPa



Iron in Slug Catcher at Troll



pH and $NaHCO_3$ in slug catcher at Troll



Prediction of Scale Potential in Ethylene Glycol (MEG) containing Solutions.

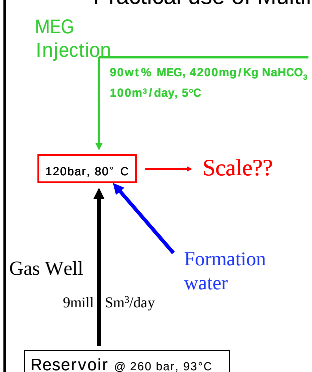
MEGscale developed for the Snøhvit and Ormen Lange gas fields

STATOIL

HYDRO

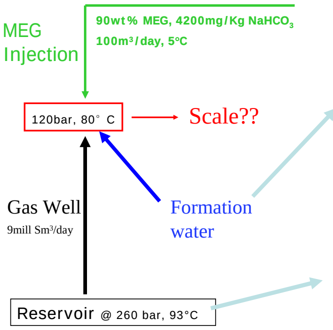
Petrotech

Practical use of MultiMEGScale



- **Want to calculate Scale potential in MEG injection point**
  - How much formation water can be accepted?

Practical use of MultiMEGScale



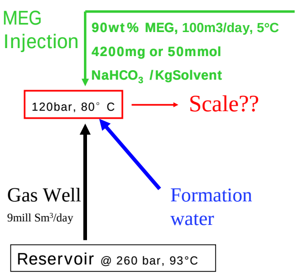
Ion	mg/l	Ion	mg/l
Na^+	58000	Cl^-	91900
K^+	730	Br^-	0
Mg^{2+}	520	SO_4^{2-}	0
Ca^{2+}	300		
Ba^{2+}	6		
Sr^{2+}	0		
Fe^{2+}	0		
Organic acid		0	mg/l
Total alkalinity		410	mg/l
Pressure		1	bar
Temperature		15	°C
pH		NA	

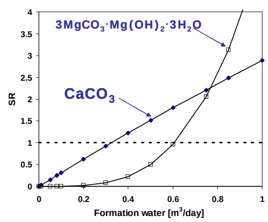
Comp	Mol (%)	MW (g/mol)	Density (kg/Sm3)
H2O	0.000	18.016	999.0
N2	2.000	28.014	0.0
CO2	1.100	44.010	0.0
H2S	0.000	34.000	0.0
C1	92.000	16.043	0.0
C2	[illegible]	30.070	0.0
C3	0.700	44.097	0.0
iC4	0.200	58.124	0.0
nC4	[illegible]	58.124	0.0
iC5	0.110	72.151	0.0
nC5	0.070	72.151	0.0
C6	0.020	86.178	664.0
C7	0.120	96.000	738.0
C8	0.050	107.000	765.0
C9	0.040	121.000	781.0
C10	0.090	134.000	792.0

Total 100

Want to calculate Scale potential in MEG injection point

- How much formation water can be accepted?
- High MEG, High alkalinity, T and P variations, Ca and Mg in formation water





Conclusion: Very little formation water can be accepted < 0.3m³/d

Pipeline chemistry

- Gas is not dried -> water condensation as temperature decreases
- Hydrate inhibition
  - Continuous injection of **M**ono **E**thylene **G**lycol (**MEG**)
  - Minimum concentration of about 60 wt%
- Corrosion
  - MEG is pH stabilised – $NaHCO_3$ is added to increase pH

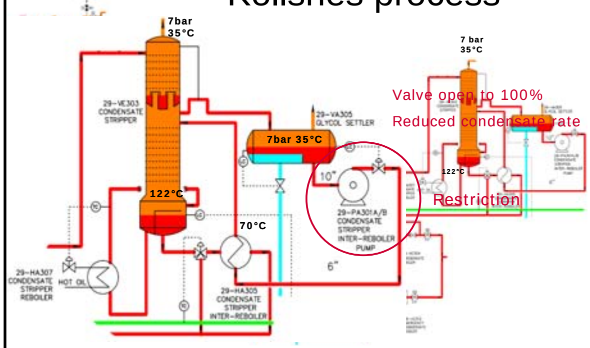
$$CO_2 + H_2O = H^+ + HCO_3^-$$
$$HCO_3^- = H^+ + CO_3^{2-}$$
$$Fe^{2+} + CO_3^{2-} = FeCO_3\,(s)$$

  - A thin layer of $FeCO_3$ is formed on pipeline wall. **Prevents further corrosion**
  - Concentration of $NaHCO_3$ 190 mmol/l **Corresponds to an alkalinity of 11 600 mg/l as HCO_3^-**

Composition of Rich MEG

Component	Concentration (mg/l)
Na+	5 032
K^+	44
Mg^{2+}	
Ca^{2+}	5
Ba^{2+}	
Sr^{2+}	
Fe^{2+}	16
Cl^-	1 000
Br^-	
SO_4^{2-}	
Alkalinity (mmol/l)	191
Alkalinity (mg/l as HCO_3^-)	11 600
MEG concentration (wt%)	66

Kollsnes process



Valve replacement

- What caused the restriction?
  - Failure of valve
  - Organic? Scale?
- Shutdown of Kollsnes **(inluding Troll, Kvitebjørn and Visund)**
  - Valve replaced
- SCALE **$NaHCO_3$**
  - From the pH stabiliser

Questions to a task force,
Baard Kaasa* and colleges at Statoil,
was asked to find the reason to the problem

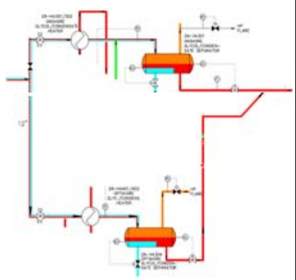
* **Responsible for the MultiMEGScale development at NTNU**

- Why scale in a condensate system?
- Why now after several years of operation?
- Why $NaHCO_3$ – a salt with high soluble in water-MEG solutions?
- How to remove it without shutting down the production?
  - **A wash/replace will require 8-12 hours -> loss of 50-70 MSm³ gas**
- **Which chemicals can we use that will not contaminate the condensate?**

And please hurry!
The valve is about to get plugged once more!

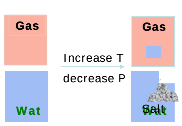
Process analysis

- Only one condensate MEG separator
  - MEG in condensate: 600 ppm
- Start of second cond-MEG separator
  - MEG in condensate: 30-40 ppm
- Improved separation, why problem?
  - **Less MEG should give less salt and less precipitation?**



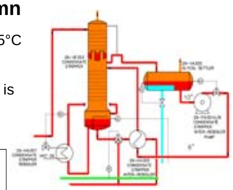
Water evaporation and salt precipitation

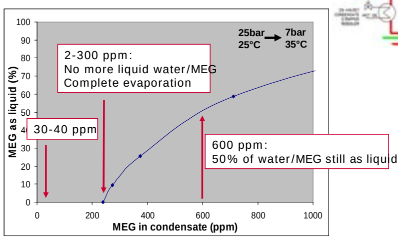
- Water and MEG are soluble in gas and oil
  - Solubility increased with higher Temp and lower Pres
- Amount of water in gas/oil is normally low compared to amount in water phase
  - Changes in water content in gas has small effect on water phase
- **BUT**, when **water fraction is small**, evaporation can change water composition significantly



MEG evaporation in stripper column

- MEG is depressurised to 7 bar and heated to 35°C
  - Solubility of MEG and water in gas increases
- What happens when MEG/water in condensate is reduced from 600 to 30-40 ppm?



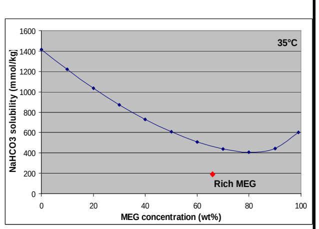


Scale removal options

- Open/replace valve
  - Require shutdown, loss of 50-70 MSm^3 gas
- Carbonate salt -> Use an acid
  - Require shutdown as acid would contaminate condensate
- Water – $NaHCO_3$ is highly soluble
  - Possible, but will increase water content in condensate
  - May cause hydrate formation in condensate transfer line
- What about using MEG?

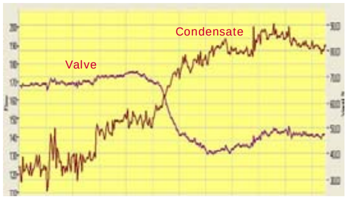
Use of MEG to dissolve scale

- $NaHCO_3$ is soluble in MEG
- Advantages with MEG
  - Already present and will not contaminate the condensate
  - Will not cause a hydrate problem
  - Clean MEG available on site
  - No use of other chemicals
  - Spent MEG can be treated in MEG regeneration
  - No waste product or outlet
- 40 l/hr MEG was injected in Condensate stripper for 24 hrs
- What happened?



Result

- Immediate increase in condensate rate
- Valve could be closed back to normal opening
- Analysis of spent MEG showed high concentrations of $NaHCO_3$
  - + some of all other ions



Summary $NaHCO_3$

- Valve in condensate stripper at Kollsnes plugged with $NaHCO_3$
  - MEG content 600 –> 30-40 ppm after startup of second condensate MEG separator
  - Complete evaporation of MEG phase in stripper – salt precipitation
- Treatment:
  - Inject MEG in condensate upstream stripper
  - Immediate removal of salt
  - Frequency: 1-2 times every month, in periods every week
- Method is very effective, simple, no-cost and no production loss
  - No contamination of condensate
  - No spill to environment – spent MEG is regenerated

A success story thanks to:
- Understanding of the fundamental chemistry of MEG systems
- Close cooperation between research centre and Kollsnes engineers
- Access to simulation tools and solubility data

Summary $CaCO_3$

- **Production of gas / condensate from a high P, T reservoir is almost impossible when formation water (FW) is produced**
  - **All salts will precipitate in the near well bore region due to full water evaporation at low FW rates.**
  - **Only very small FW rates can be tolerated before $CaCO_3$ will precipitate due to the basic water - MEG solution due to pH stabilisation.**
  - **This is the case for the two large new Norwegian gas/condensate fields**
    Snøhvite and Ormen Lange