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PRCI Research Exchange

Effect of water vapor and H_2S on the hydrogen embrittlement sensitivity of underground gas storage carbon steels assets

STORENGY

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PRCI LEADING PIPELINE RESEARCH

Pipeline Research Council International

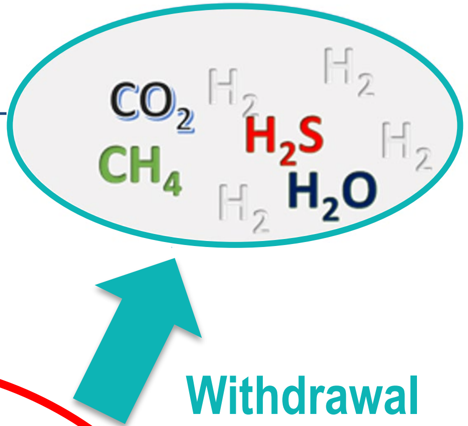
Summary

1. Context
2. State of the art
3. Materials and environmental tests
4. Water vapor and H_2S effects on the hydrogen embrittlement
5. Conclusion

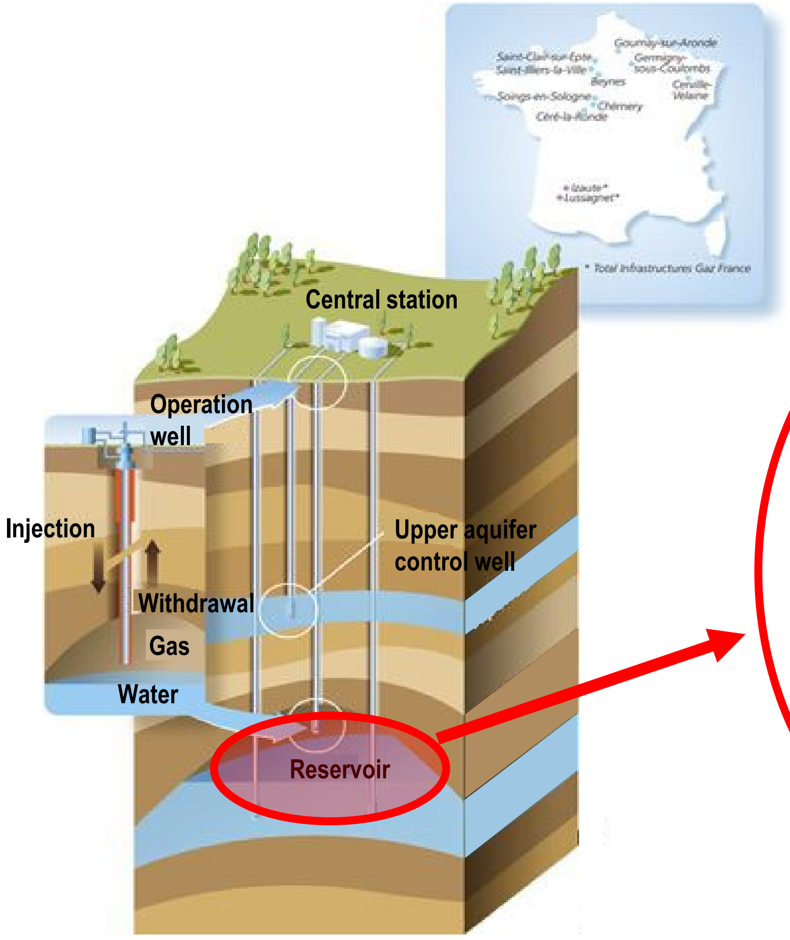
UGS & Gas Quality

- Desulfuration
- Deshydratation

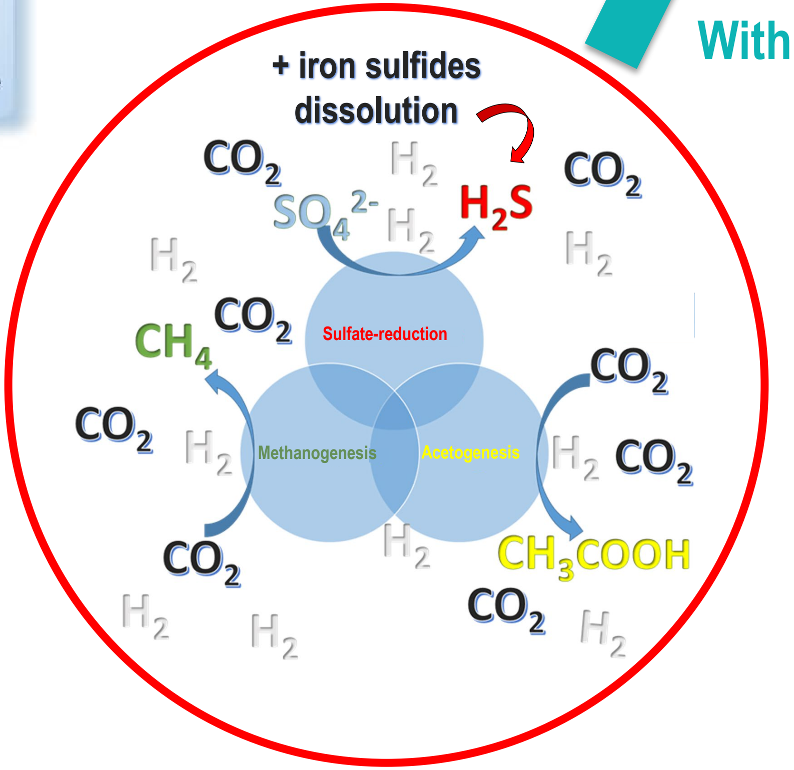
Injection into the transmission network



NG + 2% H_2	Injection	Withdrawal
Nitrogen	1.03%	1.03%
CO_2	1.06%	1.06%
Ethane (C_2H_6)	4.66%	4.66%
Propane (C_3H_8)	0.745%	0.745%
Isobutane	0.402%	0.402%
Methane (CH_4)	Balance	Balance
H_2	2%	2%
THT	24 mg/Nm^3	24 mg/Nm^3
H_2S	3.9 mg/Nm^3	30 mg/Nm^3
H_2O	< 46 mg/Nm^3	< 1000 mg/Nm^3
O_2	< 10 ppm	< 10 ppm



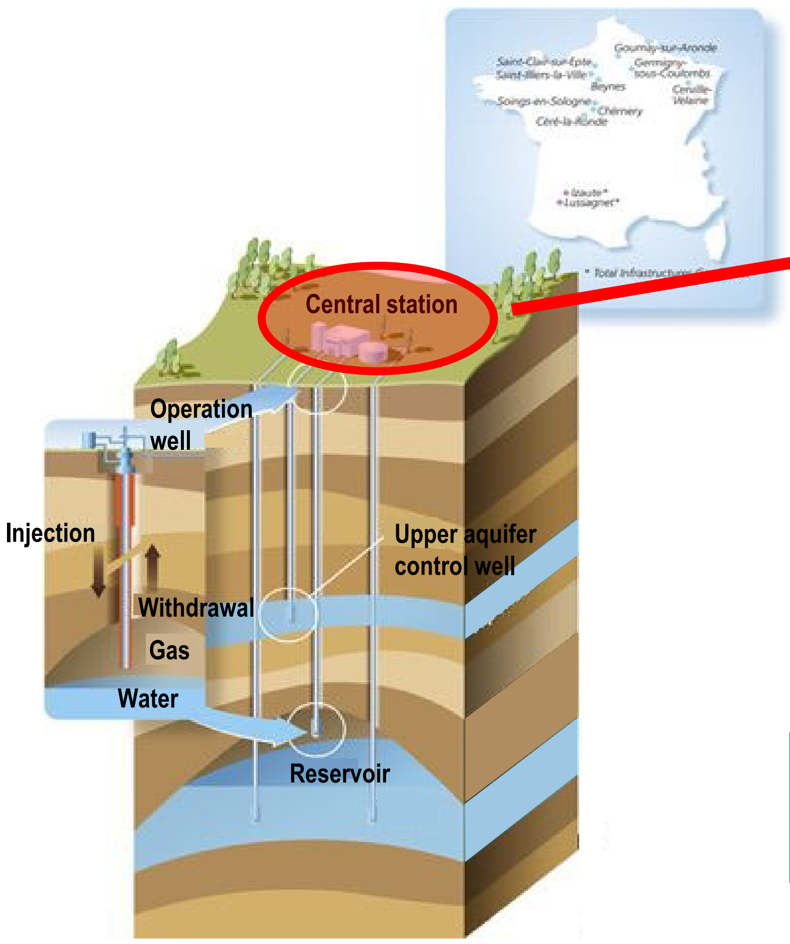
Underground aquifer gas storage



Subsurface reactions

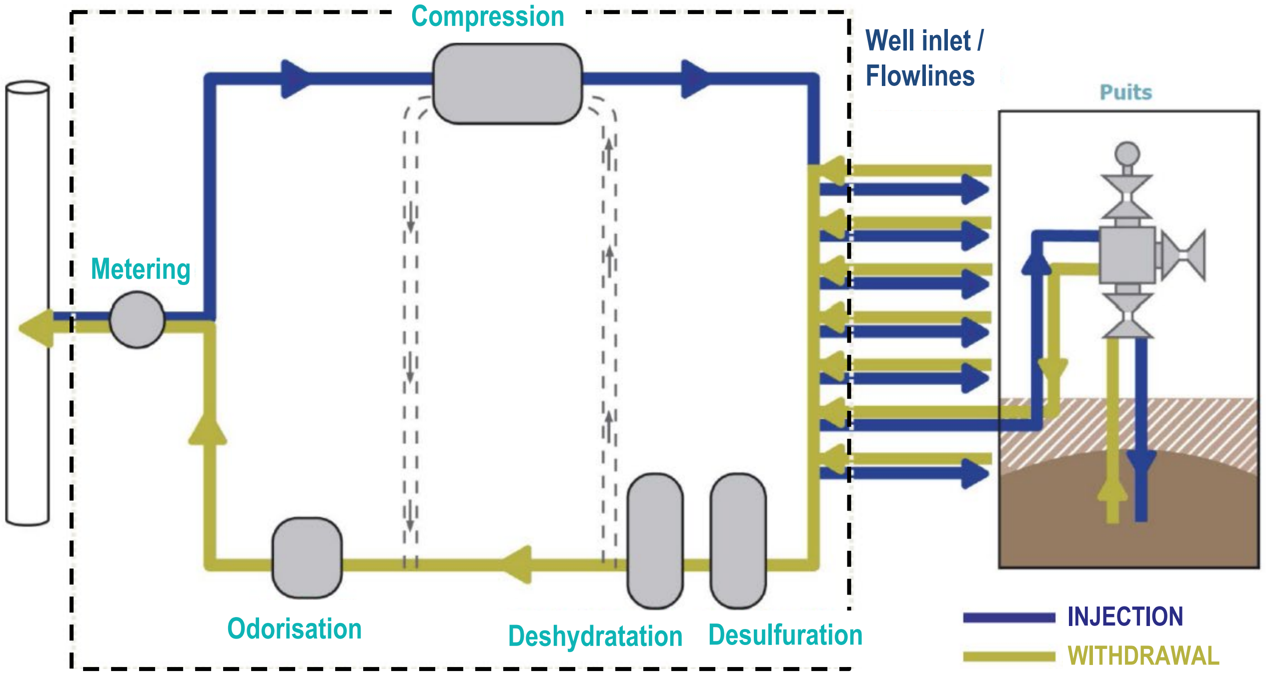
Geological H_2 storage leads to biogeochemical reactions that can significantly affect the fluids composition and thus the gas phase equilibria involved

UGS Description

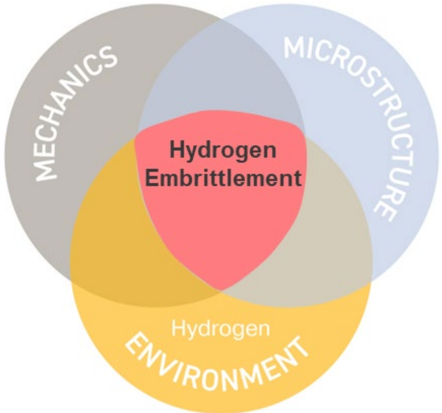


Underground aquifer gas storage

Central station



Compatibility of existing assets (surface & well) with 2%H_2-GN?



Summary

1. Context
2. **Litterature**
3. Materials and tests conditions
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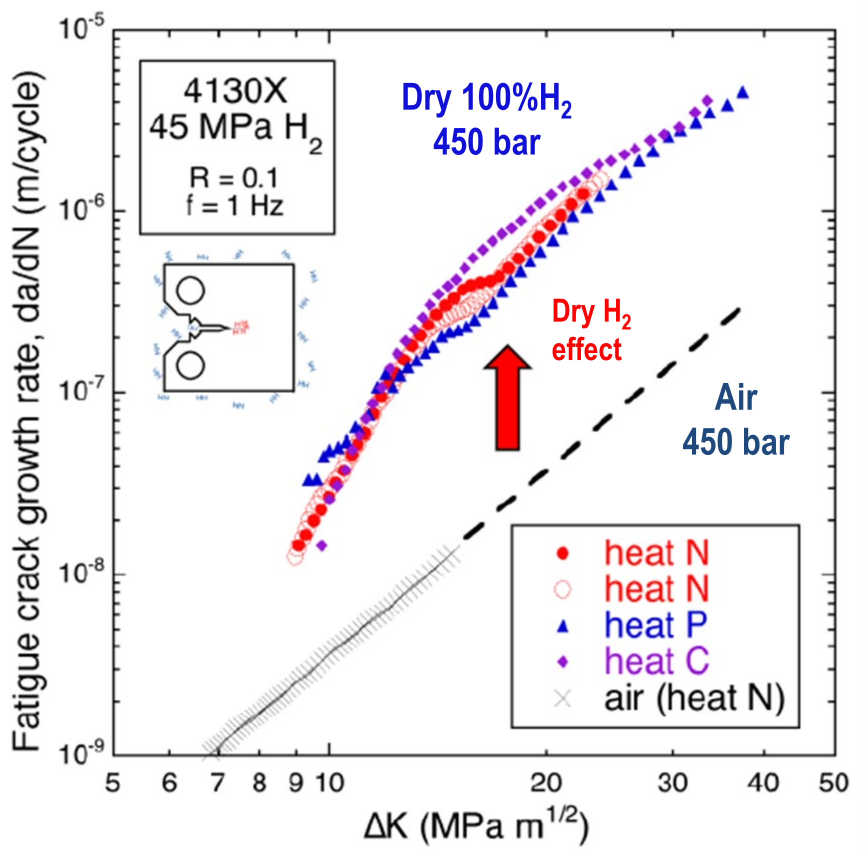
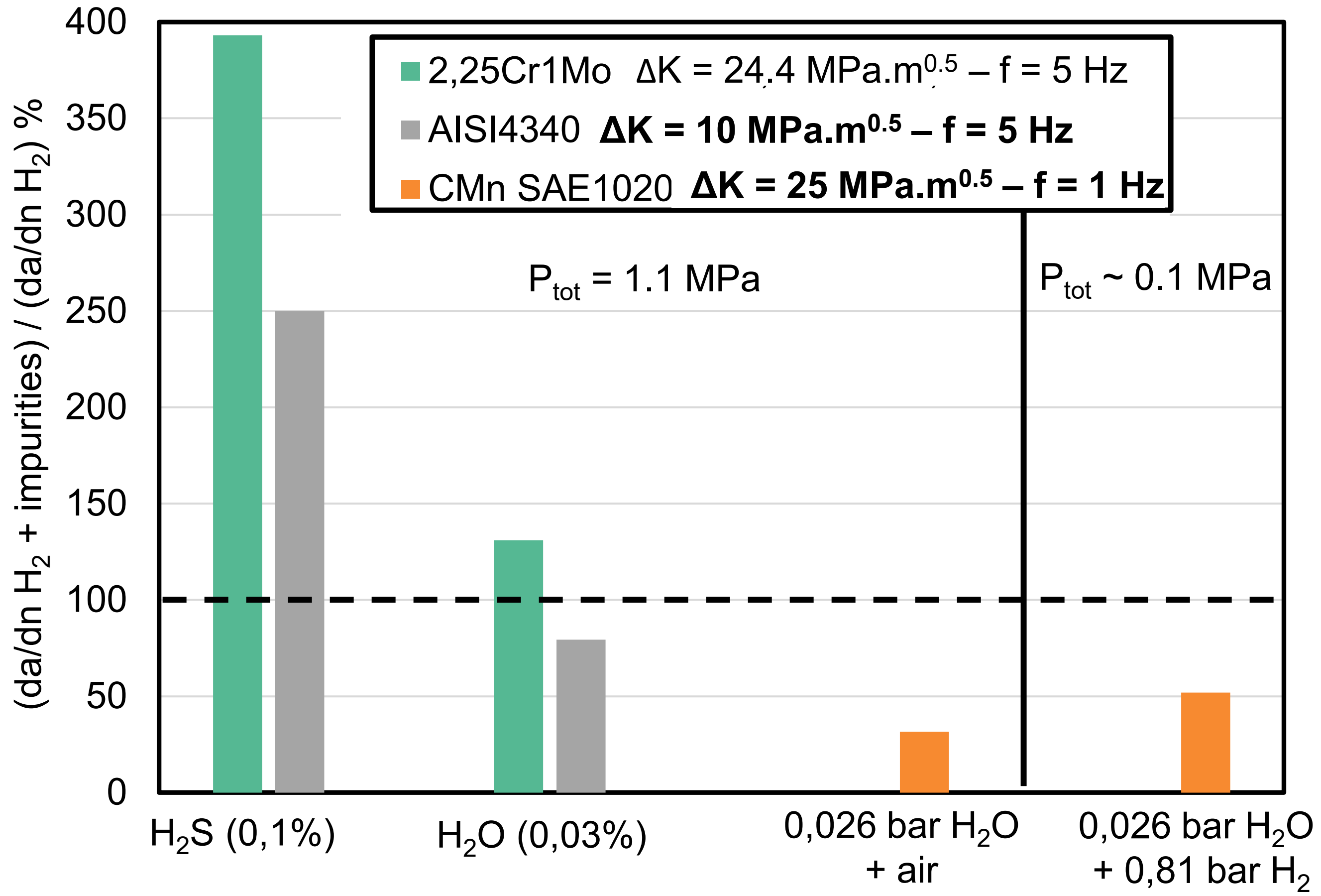
Litterature Review on the effect of H20 & H2S (scarce…)

Fatigue crack growth





S. Fukuyama, Pressure Vessel Technology, 1990
H. G. Nelson, The Metallurgical Society of AIME, 1976
K. Yokogawa, World Energy Network, 1996.

Summary

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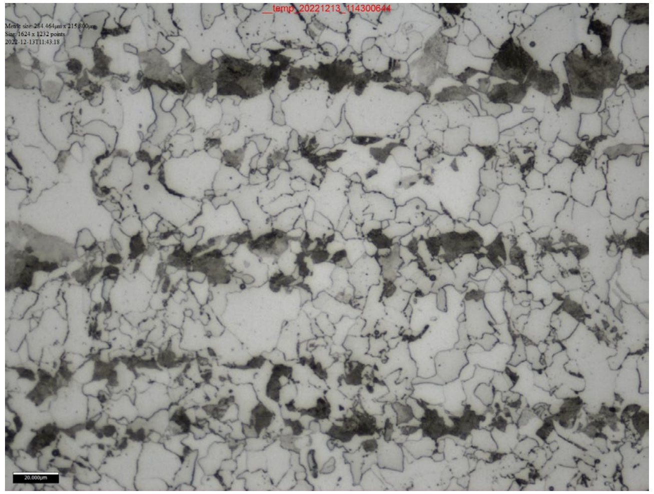
Selected UGS Materials

Seamless L360NB pipe (2009 – new) sour service

⊥ Transverse direction



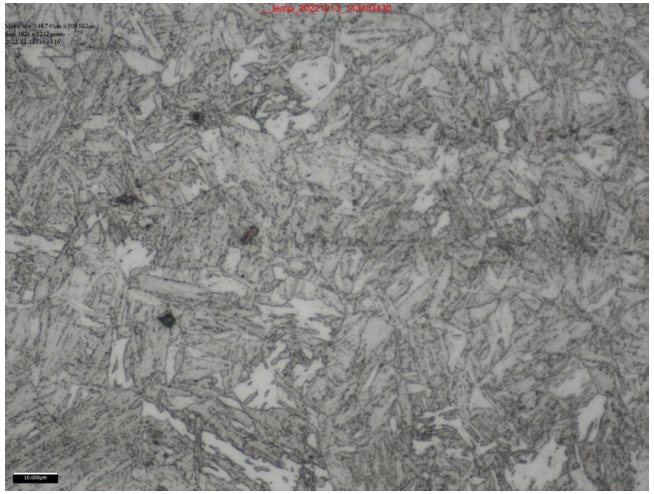
20 µm

$Rp_{0,2}$, MPa	UTS, MPa
394	538

Ferrite + perlite microstructure

Seamless N80Q tubing (2020 – new) sour service

⊥ Transverse direction



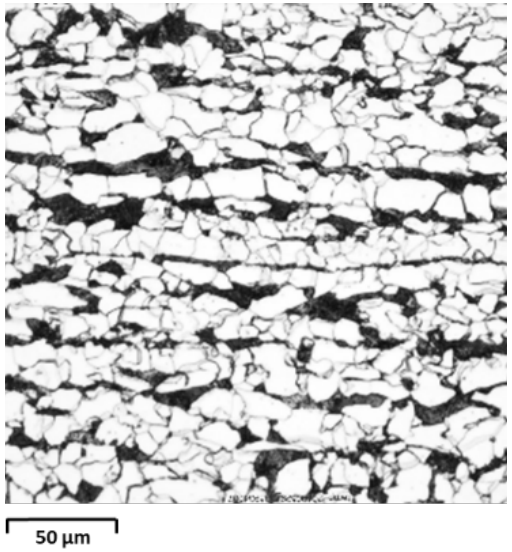
20 µm

$Rp_{0,2}$, MPa	UTS, MPa
674	761

Tempered martensite microstructure

Vintage X52 pipe (1969) non sour service

⊥ Transverse direction



$Rp_{0,2}$, MPa	UTS, MPa
430	610

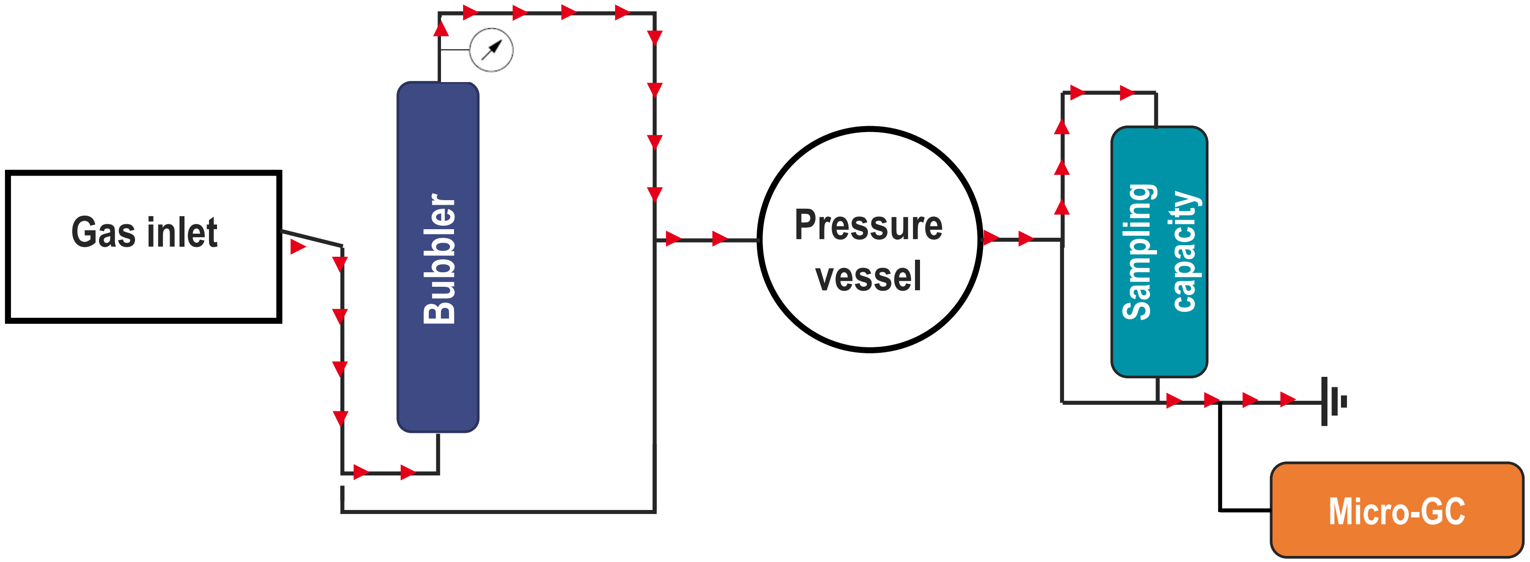
Ferrite + perlite microstructure with sulfure, alumina and oxydes inclusions

Testing environments

P_{max} = 85 bar

Wet environments (water saturated gas)				Dry environment
NG	NG + 25% H_2	NG + 27 ppmv H_2S	NG + 25% H_2 + 27 ppmv H_2S	NG + 25% H_2
P_{H2} = 0 bar	P_{H2} = 21,25 bar	P_{H2} = 0 bar	P_{H2} = 21,25 bar	P_{H2} = 21,25 bar

- In the presence of H_2S, continuous gas flow ensures a constant **H_2S content (20-25 ppmv)**
- The gas is saturated with H_2O using a bubbler (300 mg/Nm^3)



Experimental methods

Fracture toughness

- **ASTM E1820**
- **CT specimens with side grooves**
  - Thickness 10 mm : L360
  - Thickness 6 mm : N80Q
- **TL extraction direction**
- **Precrack length:**
  - a_0 = 23 mm
  - a_0/W = 0.575
- **Test ending parameter:**
  - COD_{final} = 3 mm

Fatigue crack growth

- **ASTM E647**
- **Ratio load: R = 0.1**
- **Frequency: f = 1 Hz**
- **CT specimens**
  - Thickness 10 mm : L360
  - Thickness 6 mm : N80Q
- **TL extraction direction**
- **Precracking parameters:**
  - a_0 = 23 mm
  - ΔK_{final} = 10 MPa.m^{0,5}

Thermodesorption

- **Bruker Galileo G8**
- **Charging conditions (3 h):**
  - **As-received**
  - **NG + 25%H2**
  - **NG + 25%H2 + H2S**
  - **NG + 25%H2 + H2S + H2O**

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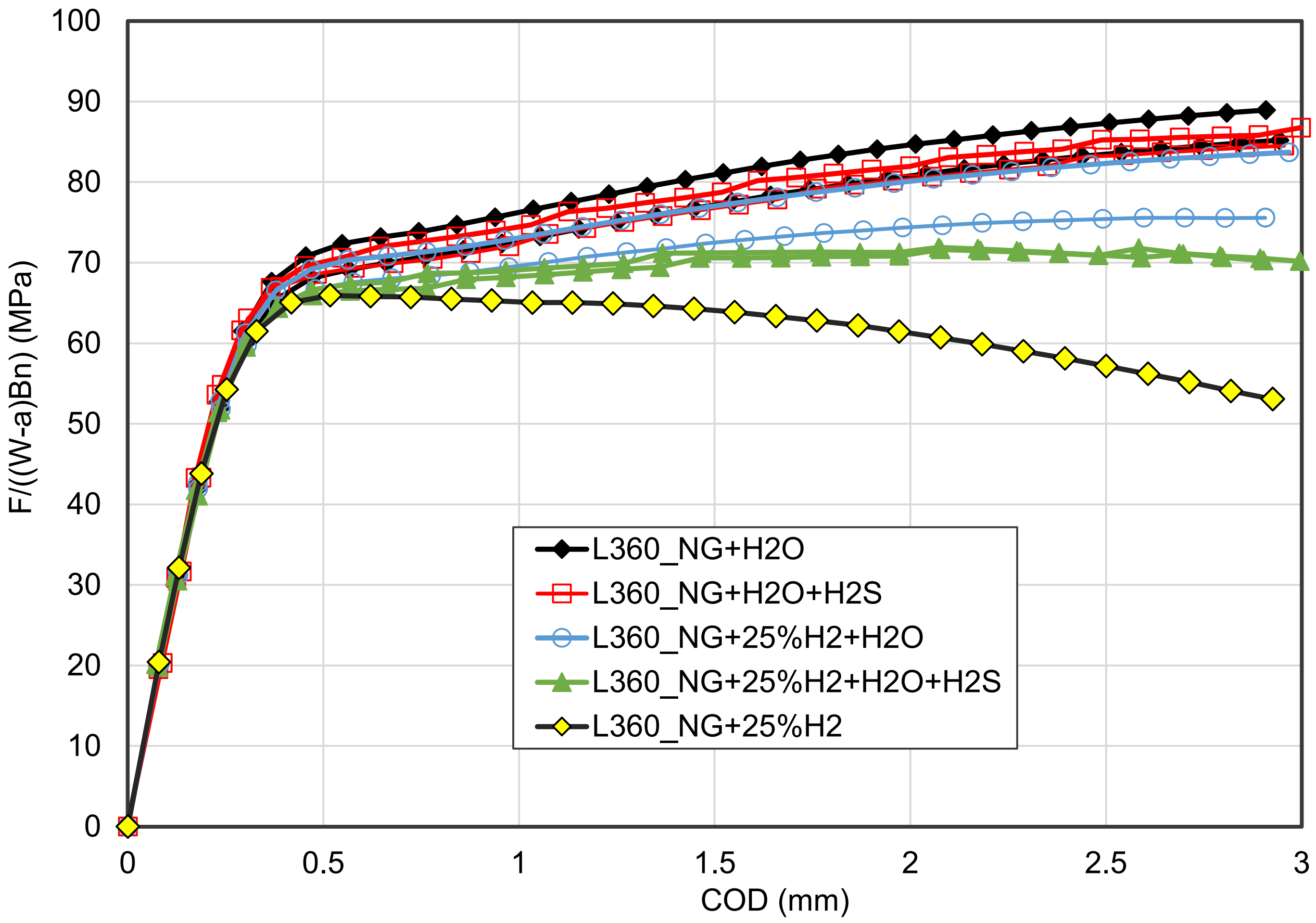
Fracture toughness: L360NB



Wet NG

Wet NG + H_2S (27 ppmv)

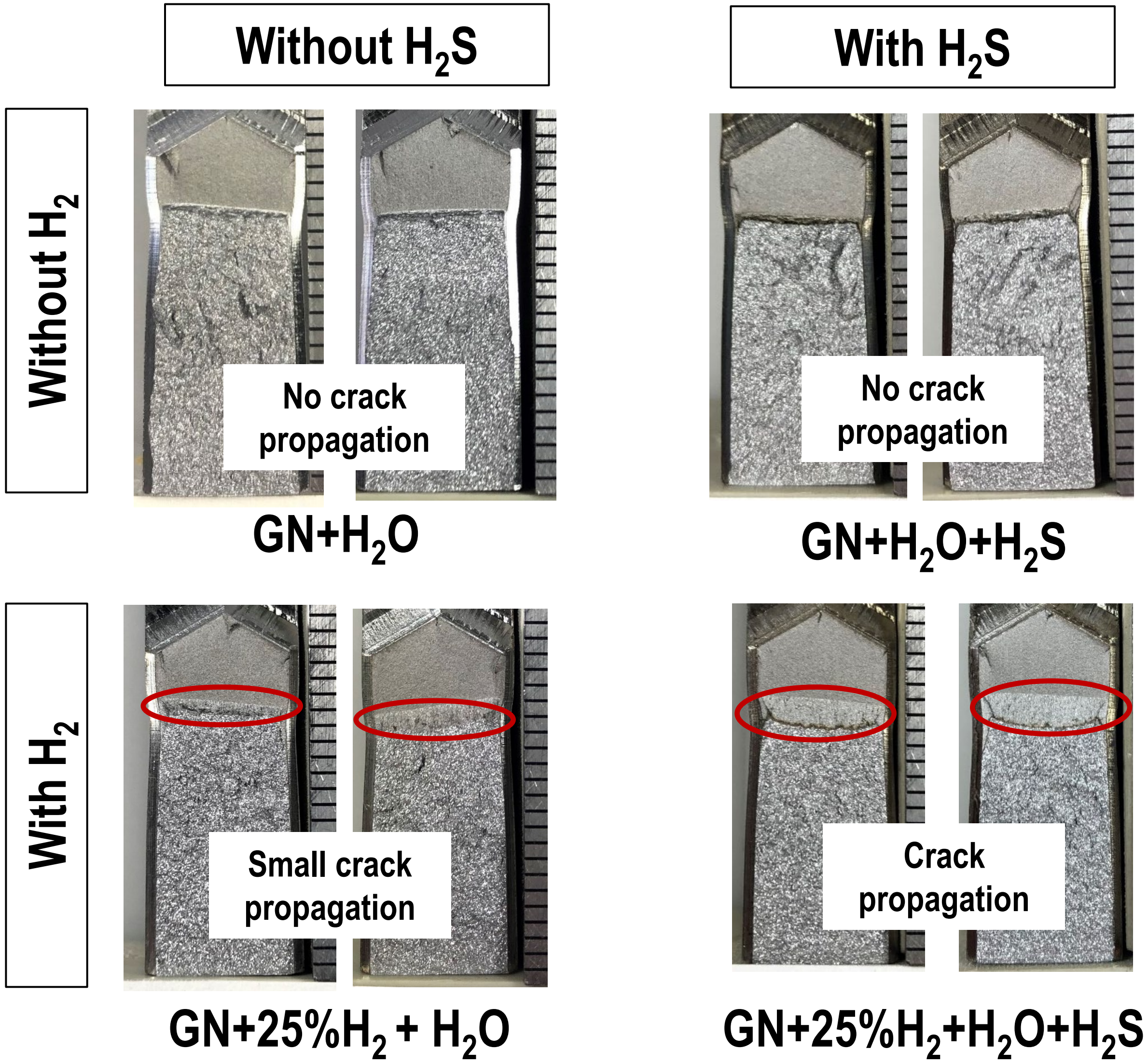
Wet 25%H_2

Wet 25%H_2 + H_2S (27 ppmv)

Dry 25%H_2

- **Synergetic effect of 25%H_2 + H_2S (27 ppmv) in wet conditions**
- **H_2O acts as an inhibitor of HE** (regarding toughness)

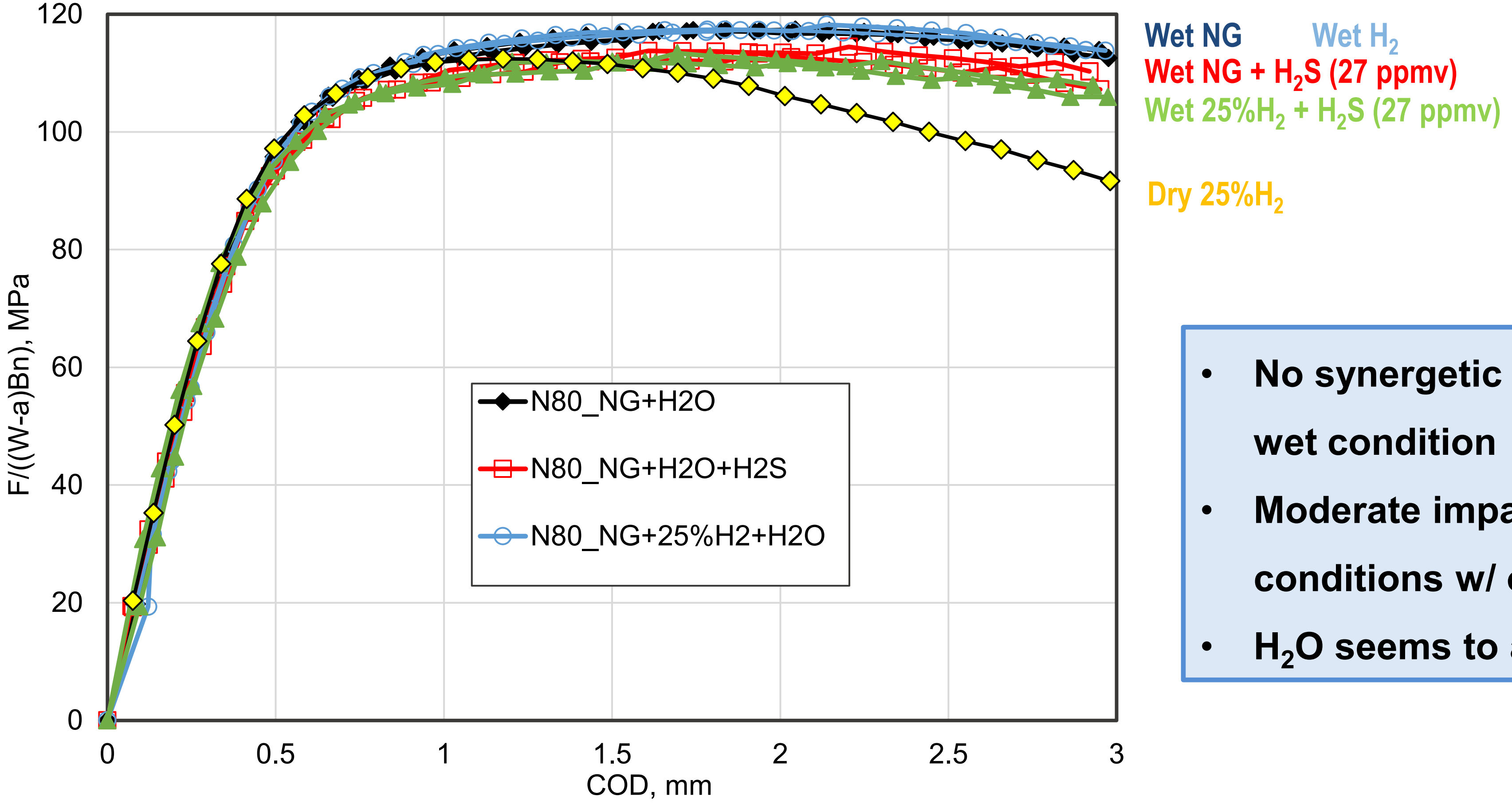
Fracture toughness: L360NB



- **Crack propagates only in the presence of H_2**
- **Synergetic effect of 25%H_2 + H_2S (27 ppmv) I wet condition**
- **H_2O acts as an inhibitor of HE, regarding FT**

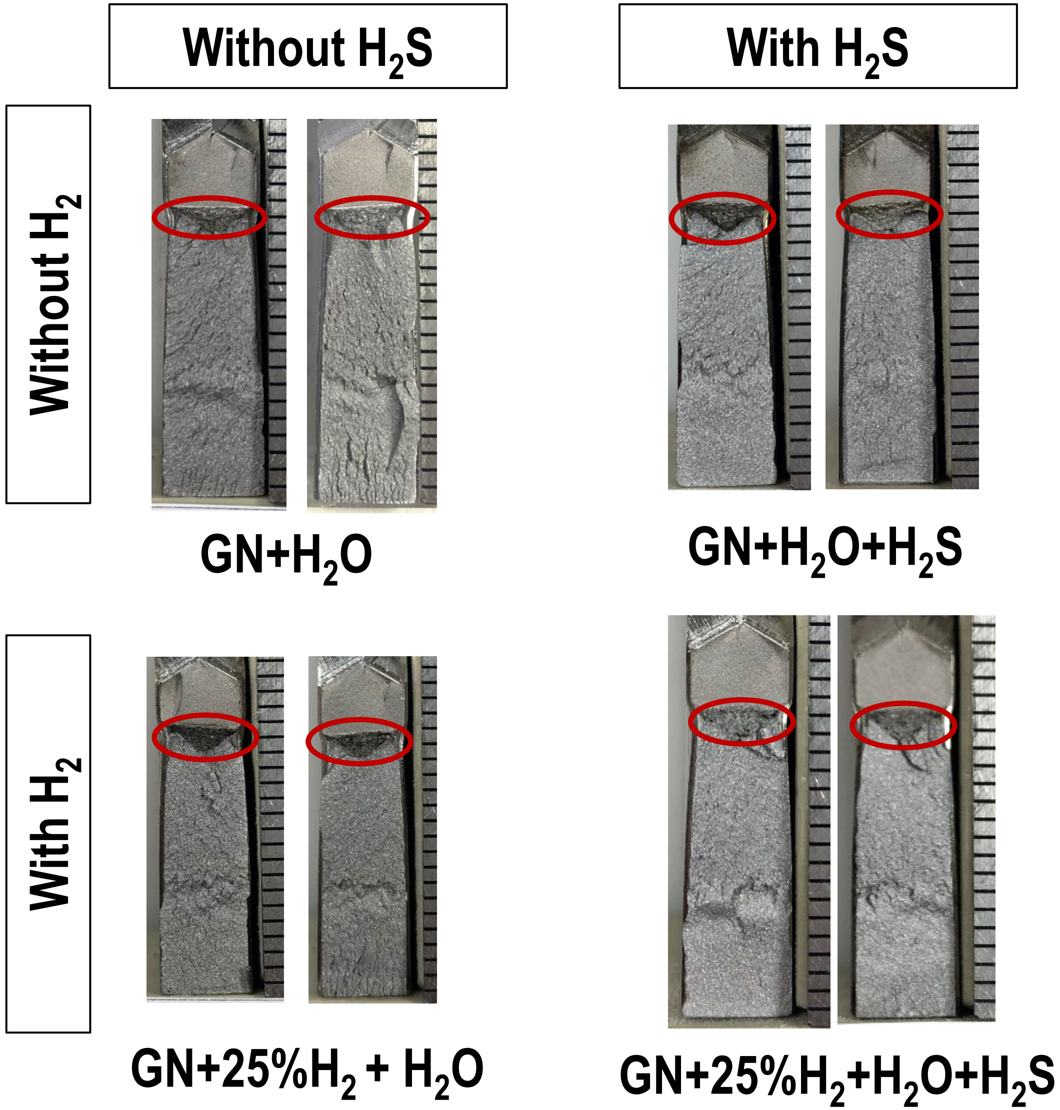
Crack propagation :

Fracture toughness: N80Q



- No synergetic effect of 25%H_2 + H_2S (27 ppmv) in wet condition
- Moderate impact of H2 on toughness in wet conditions w/ or w/o H2S
- H_2O seems to act as an inhibitor of HE

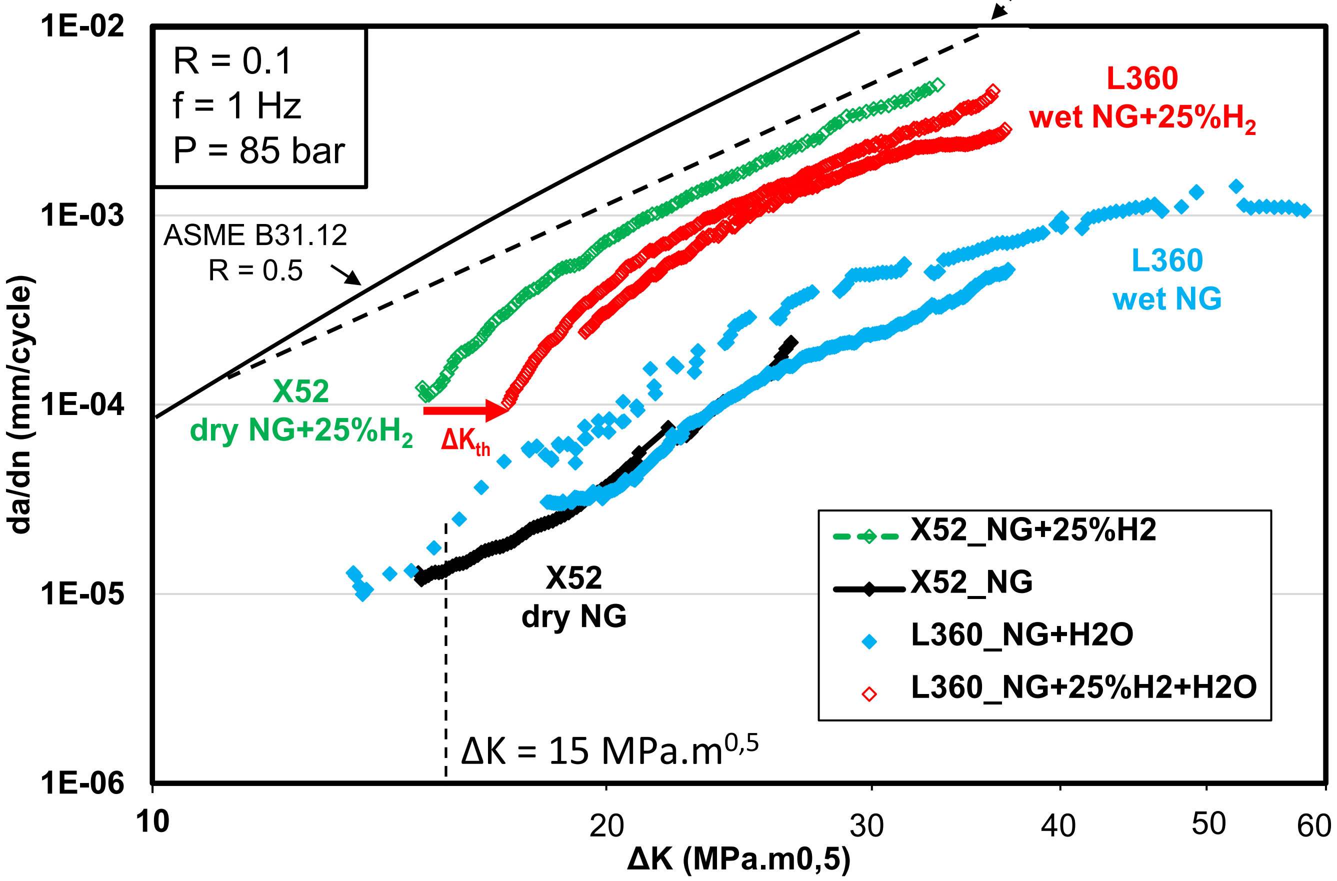
Fracture toughness: N80Q

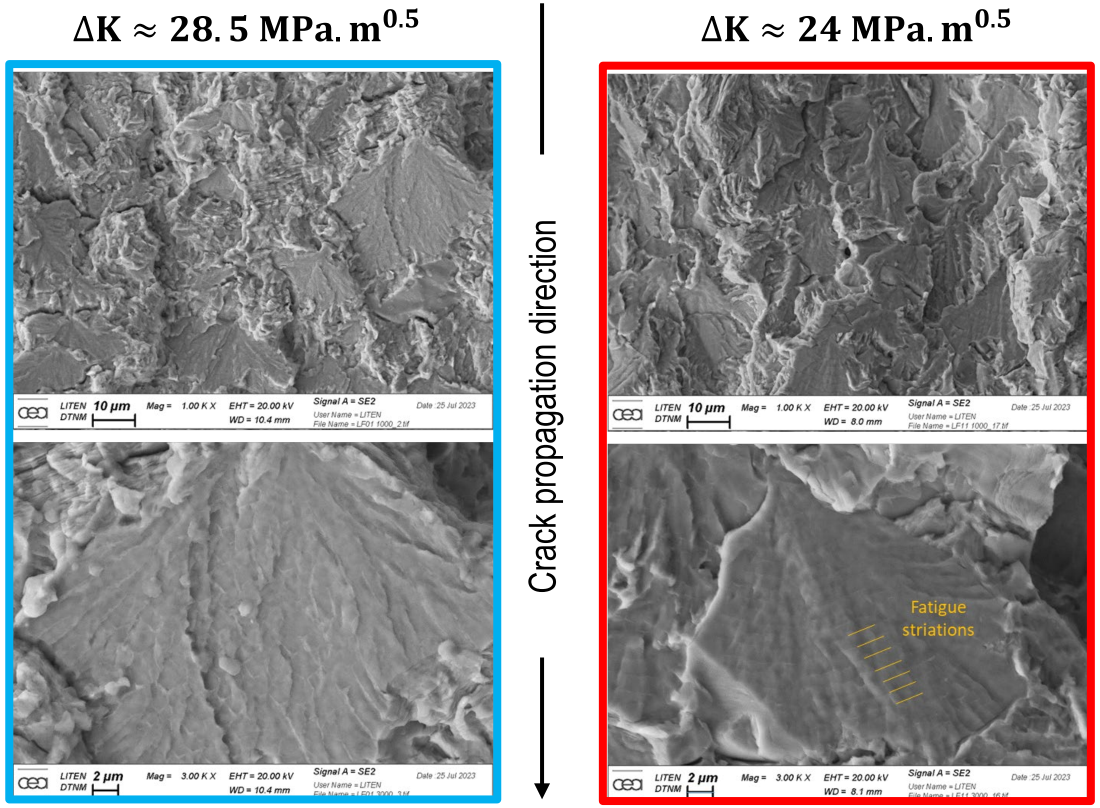


- No synergetic effect of 25%H_2 + H_2S (27 ppmv) in wet conditions
- H_2O seems to act as an inhibitor of HE
- BUT : Crack propagation in all tested conditions !

Crack propagation :

Fatigue Crack Growth (FGC): L360NB and X52

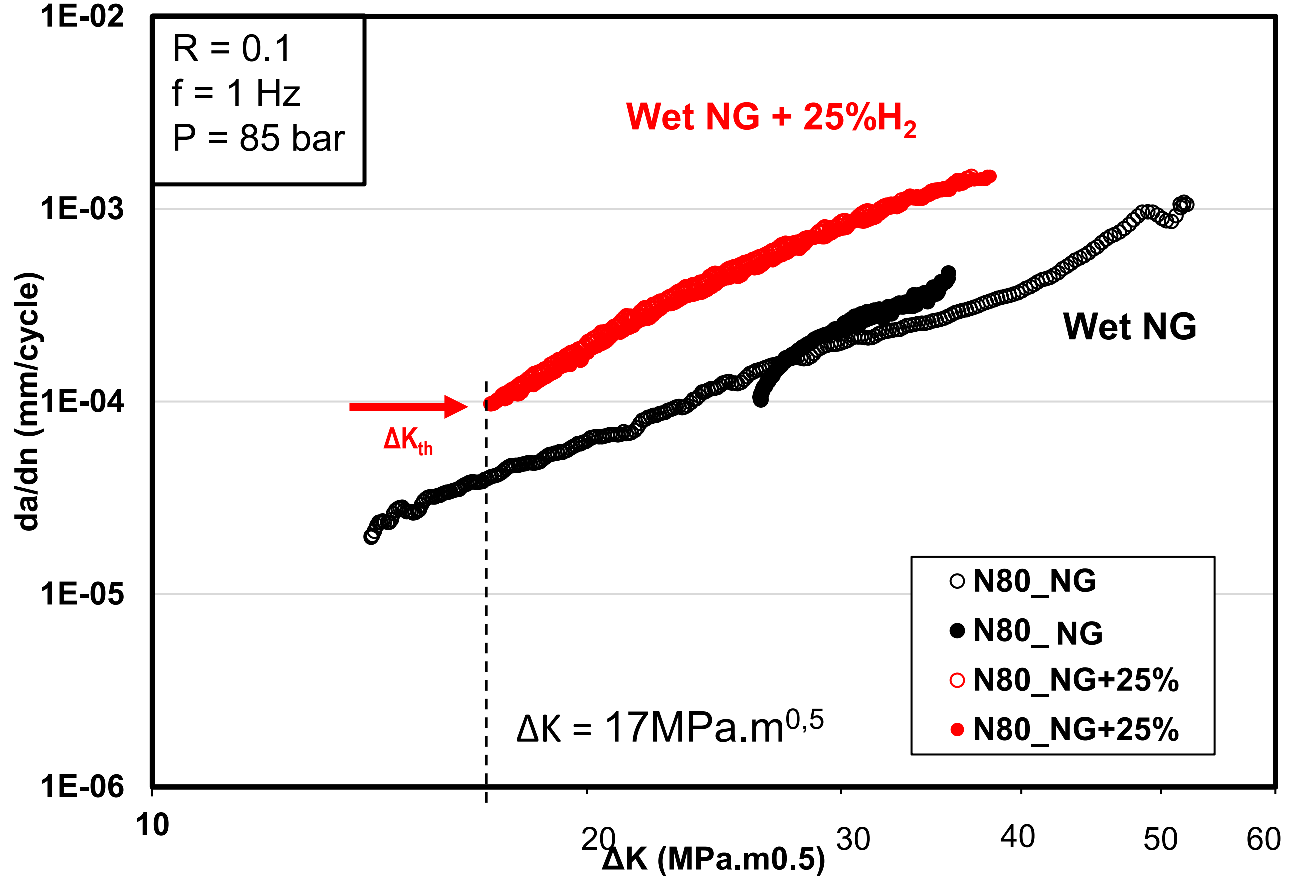




Transgranular cracking

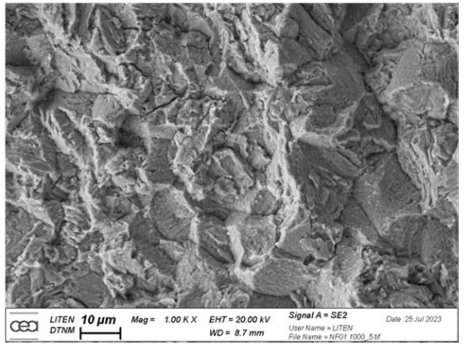
- No influence of H_2O in the Paris regime
- Influence on H_2O on ΔK_{th} shifted to higher values

Fatigue Crack Growth (FGC): N80Q



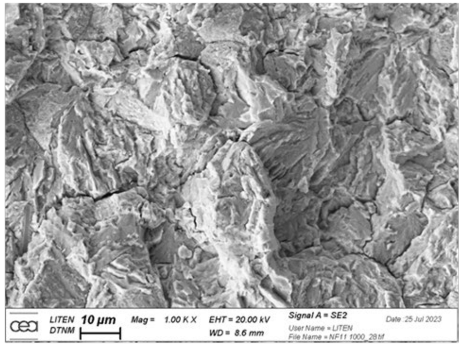
$\Delta K \approx 21.5\ MPa.m^{0.5}$

Intergranular



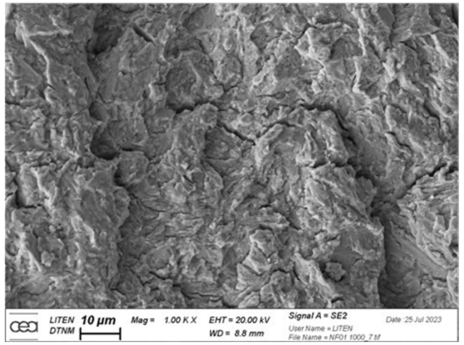
$\Delta K \approx 18\ MPa.m^{0.5}$

Transgranular



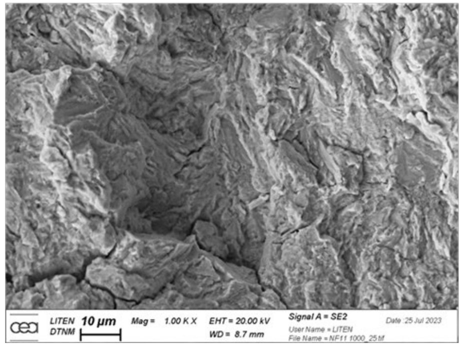
$\Delta K \approx 40\ MPa.m^{0.5}$

Transgranular



$\Delta K \approx 32\ MPa.m^{0.5}$

Transgranular



- **Increase of the FCGR with the addition of 25%H_2 in the NG saturated with water vapour but less than L360NB**
- **ΔK_{th} < 17 MPa.m^{0,5}**

Results: hot melt extraction

Loading conditions similar to those for toughness and crack propagation tests

	L360NB	N80Q
	Average	Average
As-received, wppm	0.68 ± 0.03	0.52 ± 0.28
NG +25%H_2 3h, wppm	0.44 ± 0.13	0.74 ± 0.31
NG+25%H_2+H_2S 3h, wppm	0.45 ± 0.16	0.45 ± 0.07
NG+25%H_2+H_2S+H_2O 3h, wppm	0.28 ± 0.25	0.35 ± 0.10

- Mainly H trapped is measured
- **No significant difference**
- **Does not explain H_2 + H_2O + H_2S synergy**

Discussion

- **On the influence of water vapour:**

FCG	Toughness
• ΔK_{th} shifted toward higher ΔK • Little or no effect in the Paris regime	• Inhibition of hydrogen effect

➢ *Somerday et al.* in oxygen environment: as oxygen content in hydrogen gas increased, the onset of acceleration stage was shifted toward higher ΔK. Above this ΔK threshold, the FCGR reached in 100%H_2 and in H_2 + O_2 (content < 1000 ppmv) were similar. Oxygen creates a passive layer at the metal surface, which delays hydrogen entry in the material. The passive layer coverage competes with the bare surfaces that are created as the crack propagates: once a critical fatigue crack growth rate is reached, the bare surfaces created as the crack advances cannot be entirely covered by the passive layer, leaving new surfaces unprotected toward hydrogen entry.

➢ Possible explication in our case with the assumption that O_2 and water vapor inhibiting mechanisms are similar.

- **On the synergistic effect of H_2+H_2S in wet environment:**

➢ The observation is in agreement with the scarce literature on the topic [*Kerns 1972, Fukuyama 1990, Nelson 1976*].

➢ H_2S dissolved in the water drop at the crack tip, creating locally a “sour” environment, promoting HE.

→ Capillarity condensation is the acting mechanism leading to the synergistic and detrimental effect observed

B. P. Somerday, Acta Materialia, vol. 61, no. 16, pp. 6153–6170, 2013.
S. Fukuyama, Pressure Vessel Technology, pp. 914–923, 1990.
H. G. Nelson, California 94035: The Metallurgical Society of AIME, pp. 602–611, 1976.
G. E. Kerns, Scripta Metallurgica, vol. 6, pp. 631–634, 1972.

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Conclusions

Two storage steels (N80Q and L360NB) were tested for toughness and FCGR in H2O/H2S/H2 gas:

- **Fracture toughness** behaviour of **L360NB is degraded** in the presence of **wet 25%H_2+ 27 ppmv H_2S.** H2O seems to reduce H2 impact on FT, and H2S to increase it. The combination H2/H2S/H2O brings synergy.
- **Fracture toughness** behaviour of **N80Q** is **only affected in dry 25%H_2** compared to other wet conditions.
- **FCGR** of L360NB and N80Q are **accelerated** by factor 7 and 5 respectively in the **presence of wet NG+25%H_2.** This infirms the HE inhibition by water.
- **Wet environment seems to be less severe than dry environment** for the considered alloys**. There could be a HE synergy with combination of H2O and H2S.**

QUID with higher H_2S content ?

This is not the end Folks !

We will be back…

Acknowledgements

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  - Christophe POMMIER, Storengy
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thank you

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