“Pas de deux” of high-temperature alloy and 3D reactor technology for steam cracking of coils: impact on product yields and coke formation

S.H. Symoens, M.R. Djokic, J. Zhang, G. Bellos, D. Jakobi, J. Weigandt, S. Klein, F. Battin-Leclerc, G. Heynderickx, J. Van Thielen, B. Cuenot, T. Faravelli, G. Theis, P. Lenain, A.E. Muñoz, J. Olver, K.M. Van Geem

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Outline

- Introduction
- High-temperature alloys and 3D reactor technology
    - Yields
    - Tube metal temperatures
    - Coke formation
- Conclusions

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Coke formation

Deposition of a carbon layer on the reactor surface

- ✗ Thermal efficiency
- ✗ Product selectivity
- ✗ Decoking procedures

[Muñoz, 2013]

Estimated annual cost to industry: $ 2 billion

Optimization by
- Feed additives
- Metallurgy & surface technology
- 3D reactor technology

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L. Benum, "Achieving Longer Furnace Runs at NOVA Chemicals," in AIChE Spring National Meeting, 14th Annual Ethylene Producers' Conference, New Orleans, Louisiana, 2002.

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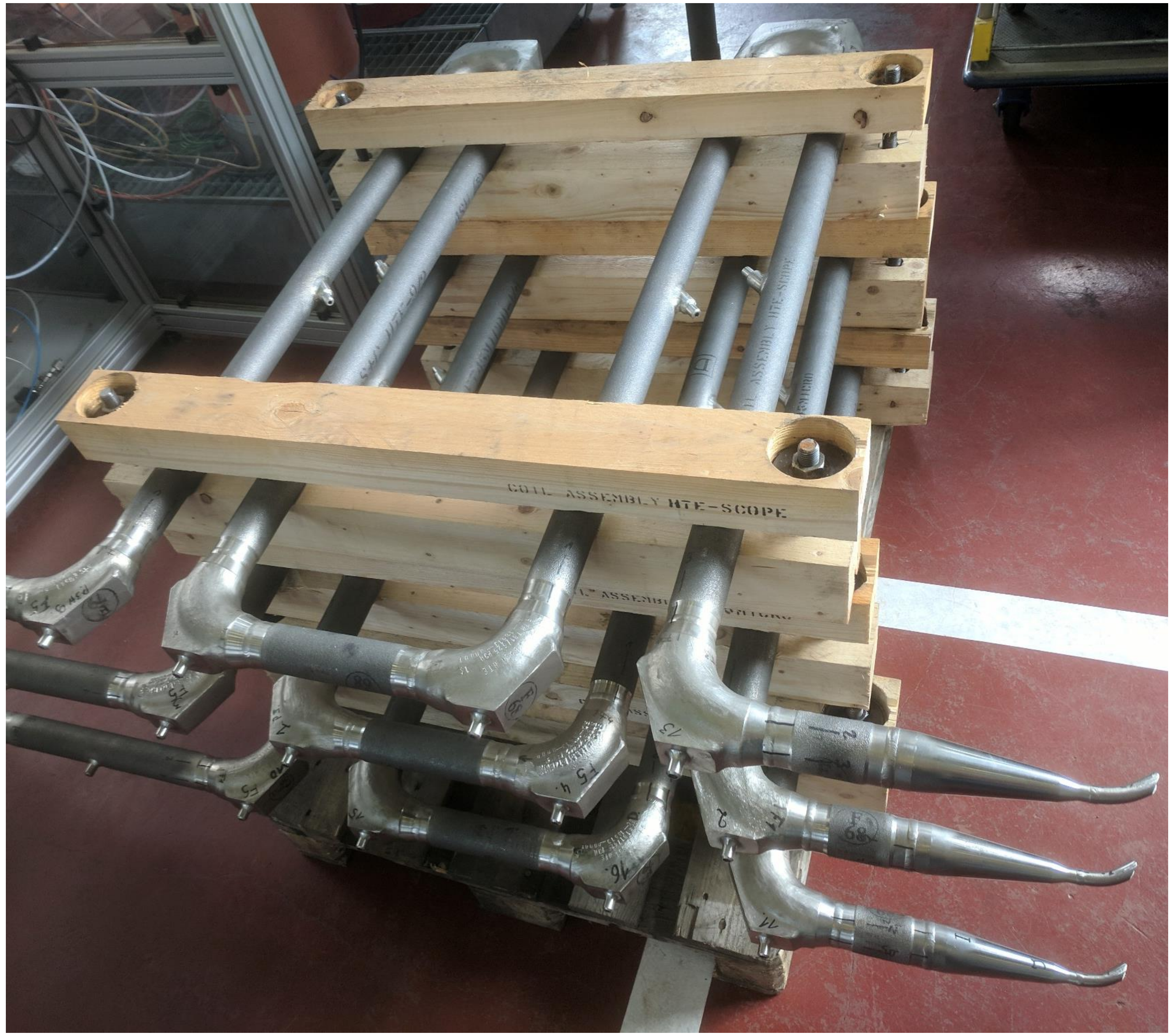
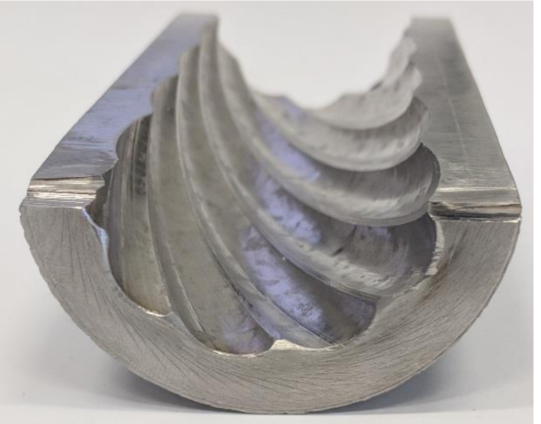
Reactors

Centralloy® ET 45 Micro

Centralloy® HT E

Centralloy® HT E + SCOPE®

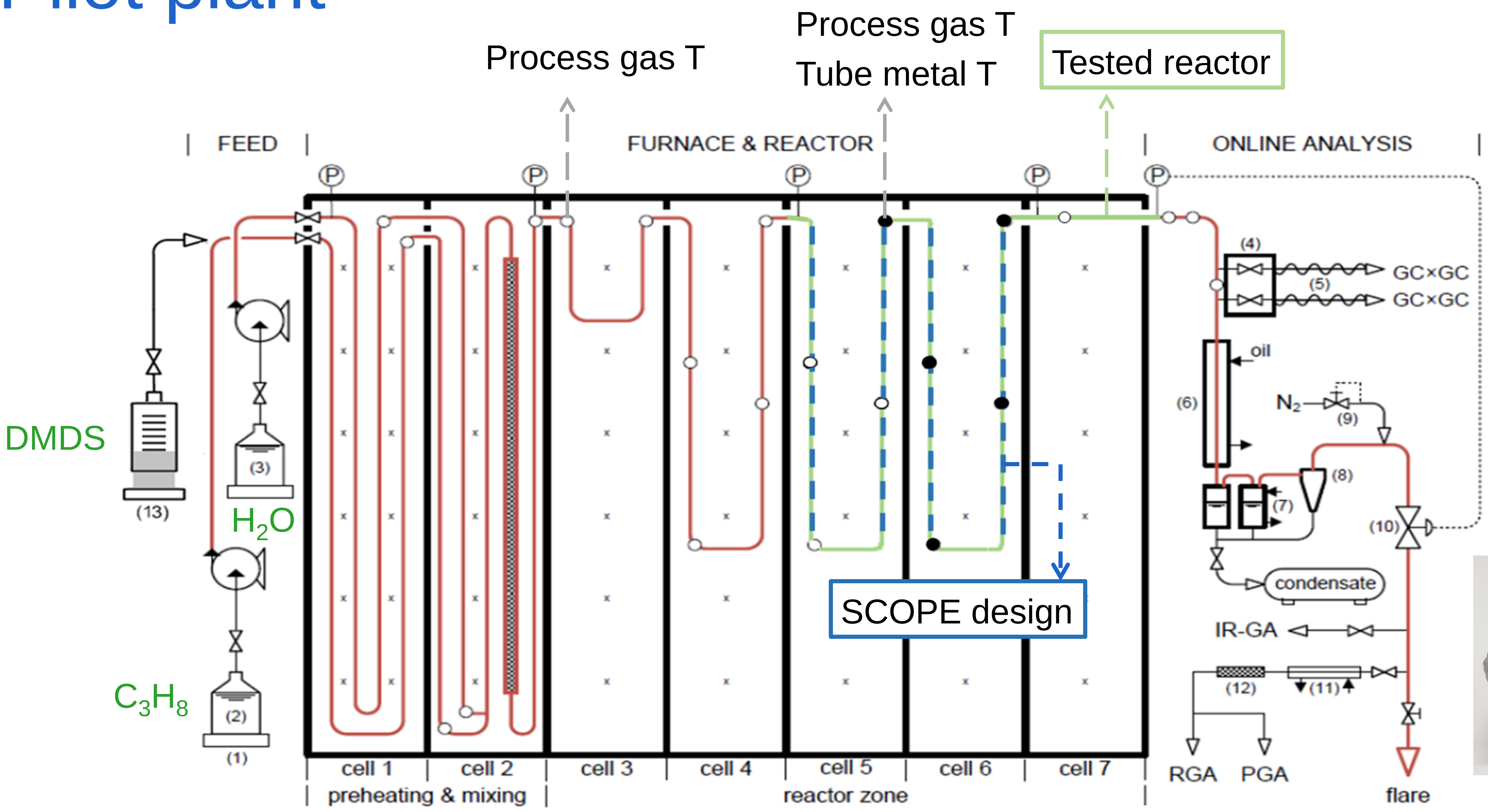


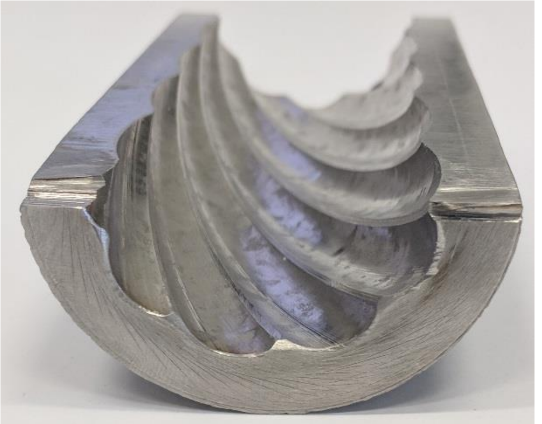


Alloy	Composition [wt %]								
	C	Si	Mn	Cr	Fe	Ni	Al	Nb	Additions
ET 45 Micro	0.45	1.6	1.0	35	bal.	45	-	1.0	MAE, RE
HT E	0.45	-	-	30	bal.	45	4.0	0.5	MAE, RE

RE: reactive elements; MAE: micro-alloying elements

Pilot plant


Process gas T
Process gas T
Tube metal T
Tested reactor
FEED
FURNACE & REACTOR
ONLINE ANALYSIS
DMDS
H_2O
C_3H_8
(13)
(3)
(2)
(1)
(4)
(5)
GC×GC
GC×GC
oil
(6)
N_2
(9)
(8)
(7)
(10)
condensate
IR-GA
(12)
(11)
RGA
PGA
flare
SCOPE design
cell 1
cell 2
cell 3
cell 4
cell 5
cell 6
cell 7
preheating & mixing
reactor zone



Experimental program

- Steam treatment for 10 hours
- 1CC: COT = base; 6 hours
- 2CC: COT = base; 2 hours
- 3CC: COT = base; 6 hours
- 4CC: COT = base + 110 °C/ + 160 °C*; 1.67 hours
- 5CC: COT = base; 12 hours

*SCOPE®

✓Decoking was performed after every Cracking Cycle (CC)
✓Prior to each CC a pre-sulfiding step was performed

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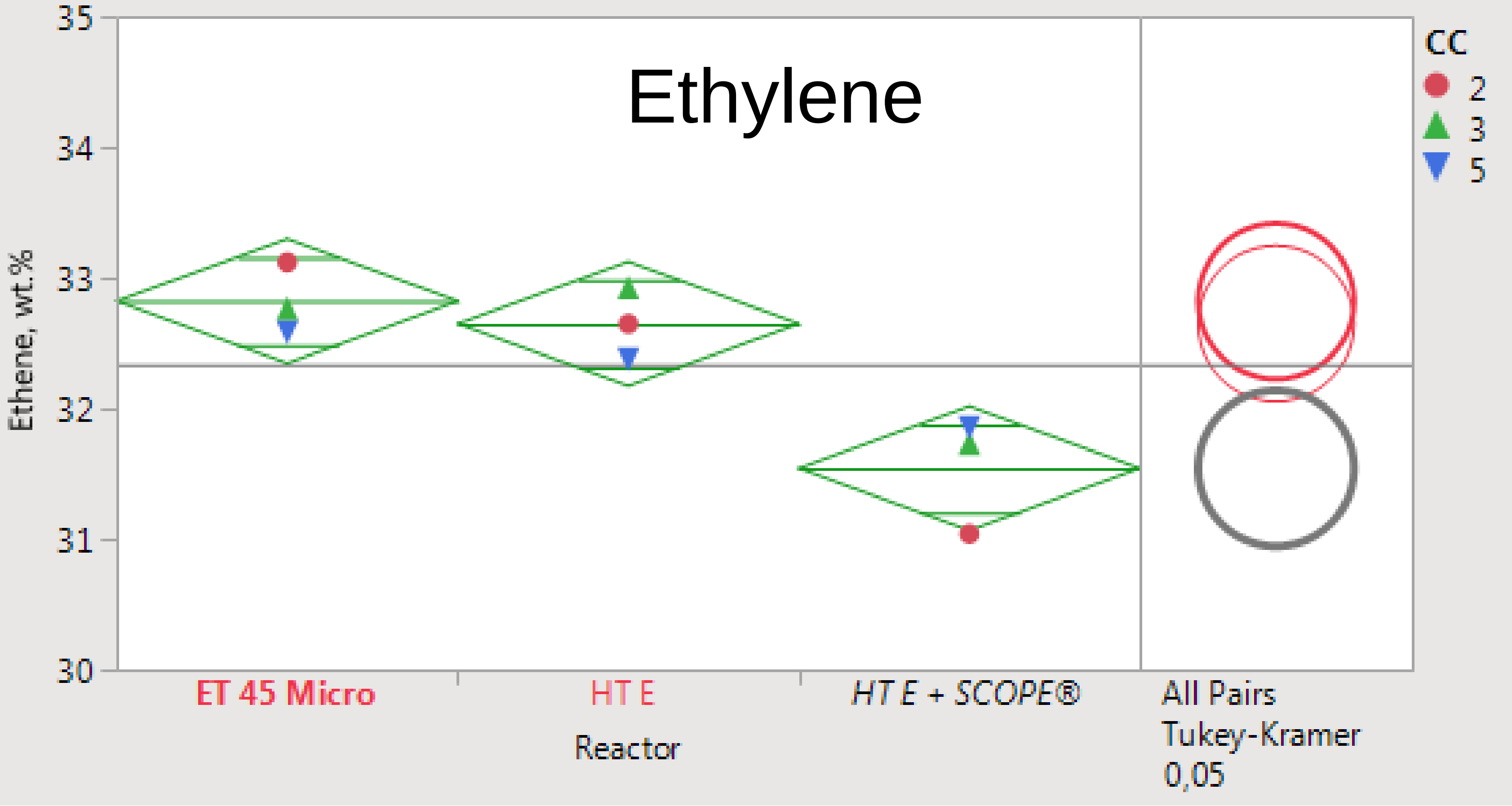
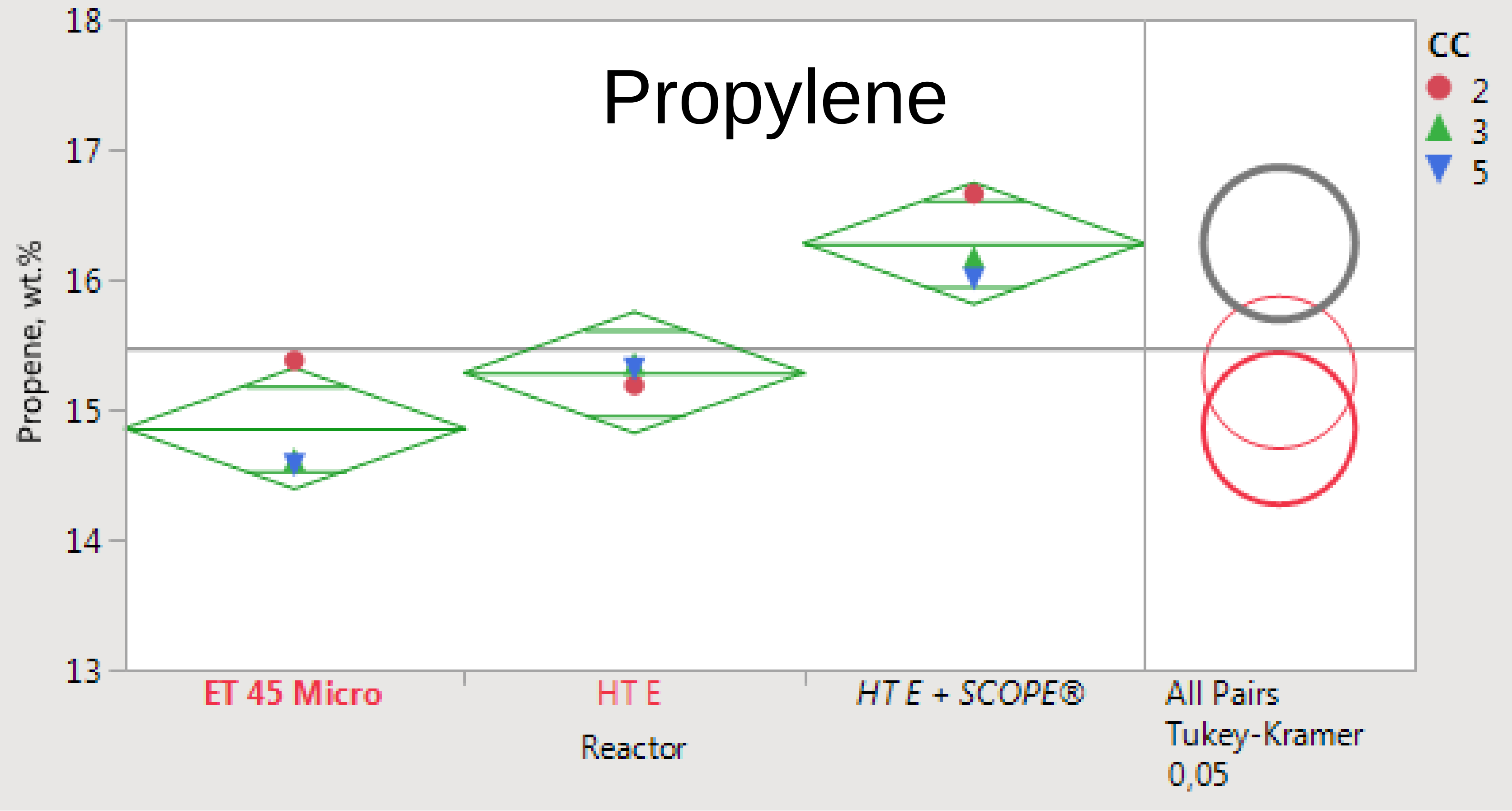
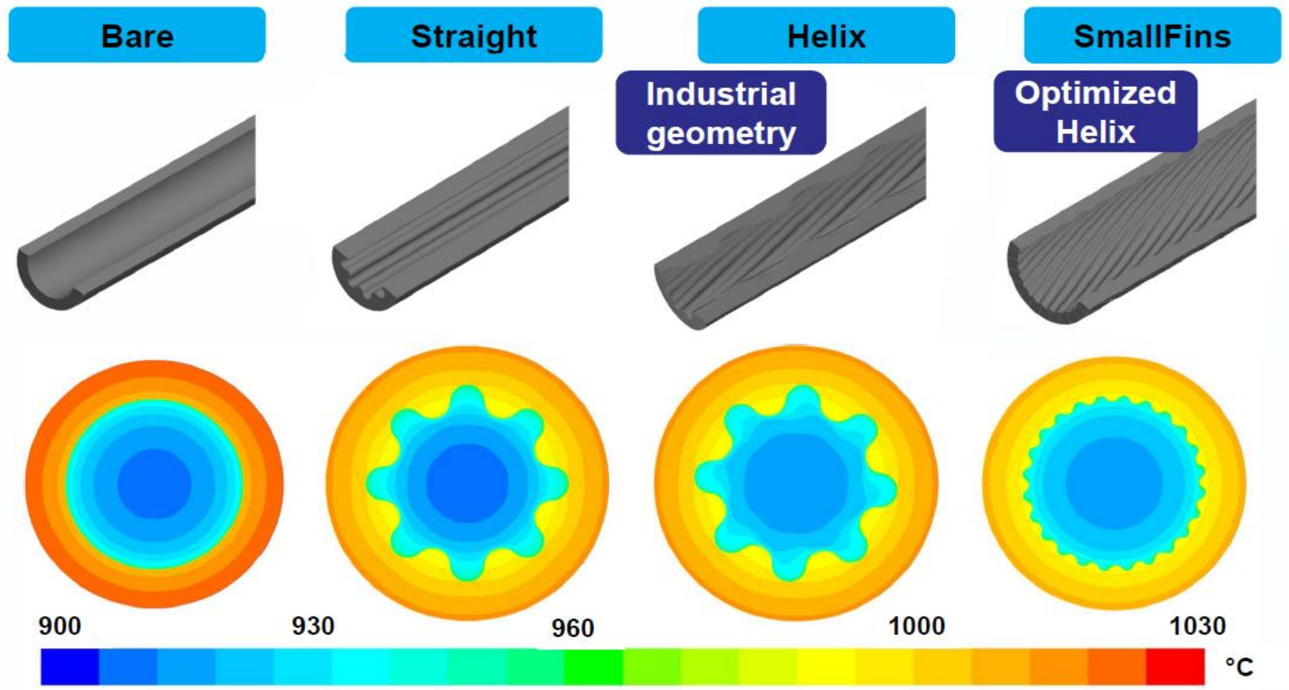
Product yields

2 (CC2), 6 (CC3) and 12 h (CC5) cracking cycles





Reduced over-cracking near wall



Schietekat, et al., "Computationally efficient CFD simulations with detailed free-radical mechanisms", in AIChE Annual Meeting, San Francisco, CA, 2013.

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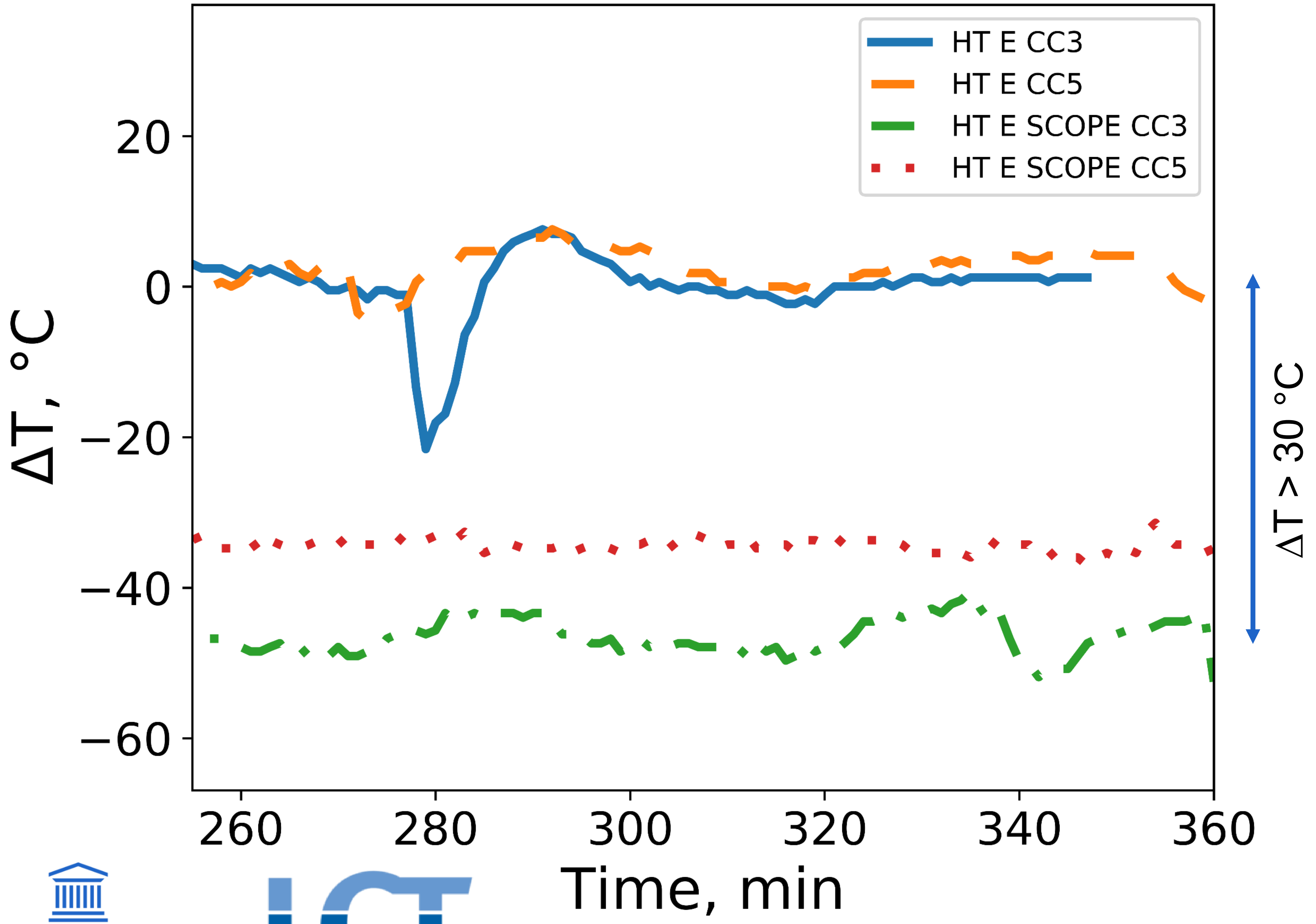
Tube metal temperatures



Pyrometer

Weld-on TC's

Manual T

Gas consumption

Result

~10 % lower

Fuel gas consumption

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Tube metal temperatures

30°C lower tube metal temperature reduces fuel consumption by ~10%

- q is constant → $T_{gas/coke}$ decreases
- $U\ A$ increases → $T_{gas/coke}$ decreases
- ↓ $T_{wall,in}$ decreases
- ↓ $T_{wall,out}$ decreases
- ↓ q_{emit} decreases
- ↓ q_{inci}, q_{conv} can decrease
- ↓ T_{refr}, T_{flue} can decrease
- ↓ $\dot{m}_{fuel}$ can decrease

Convection on inner wall $q = U\ A\ (T_{gas/coke} - T_{bulk})$

Conduction through coke $q = k_c\ A\ (T_{wall,in} - T_{gas/coke})/d_c$

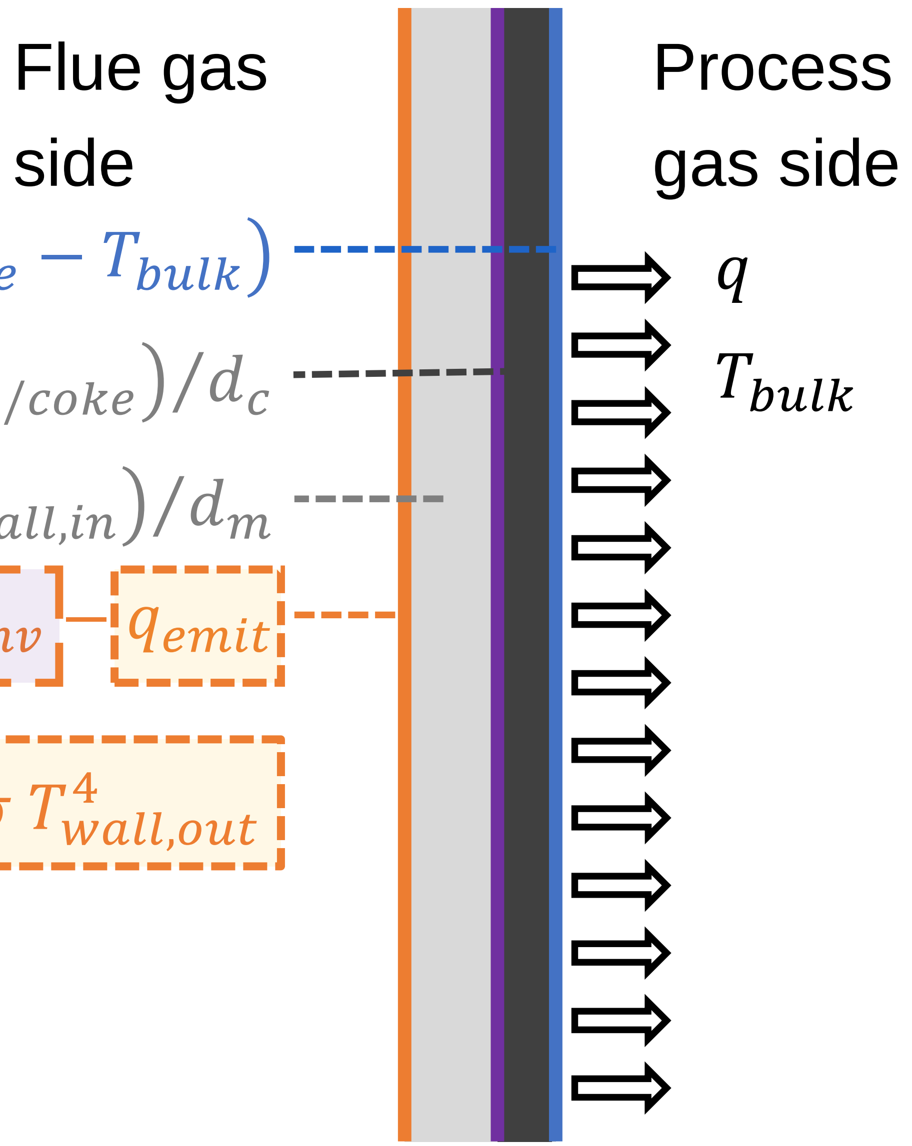
Conduction through metal $q = k_m\ A\ (T_{wall,out} - T_{wall,in})/d_m$

Heat balance on outer wall $q = q_{inci} - q_{re} + q_{conv} - q_{emit}$

$\varepsilon_w\ q_{inci} + q_{conv}$ $\quad$ $\varepsilon_w\ \sigma\ T_{wall,out}^4$

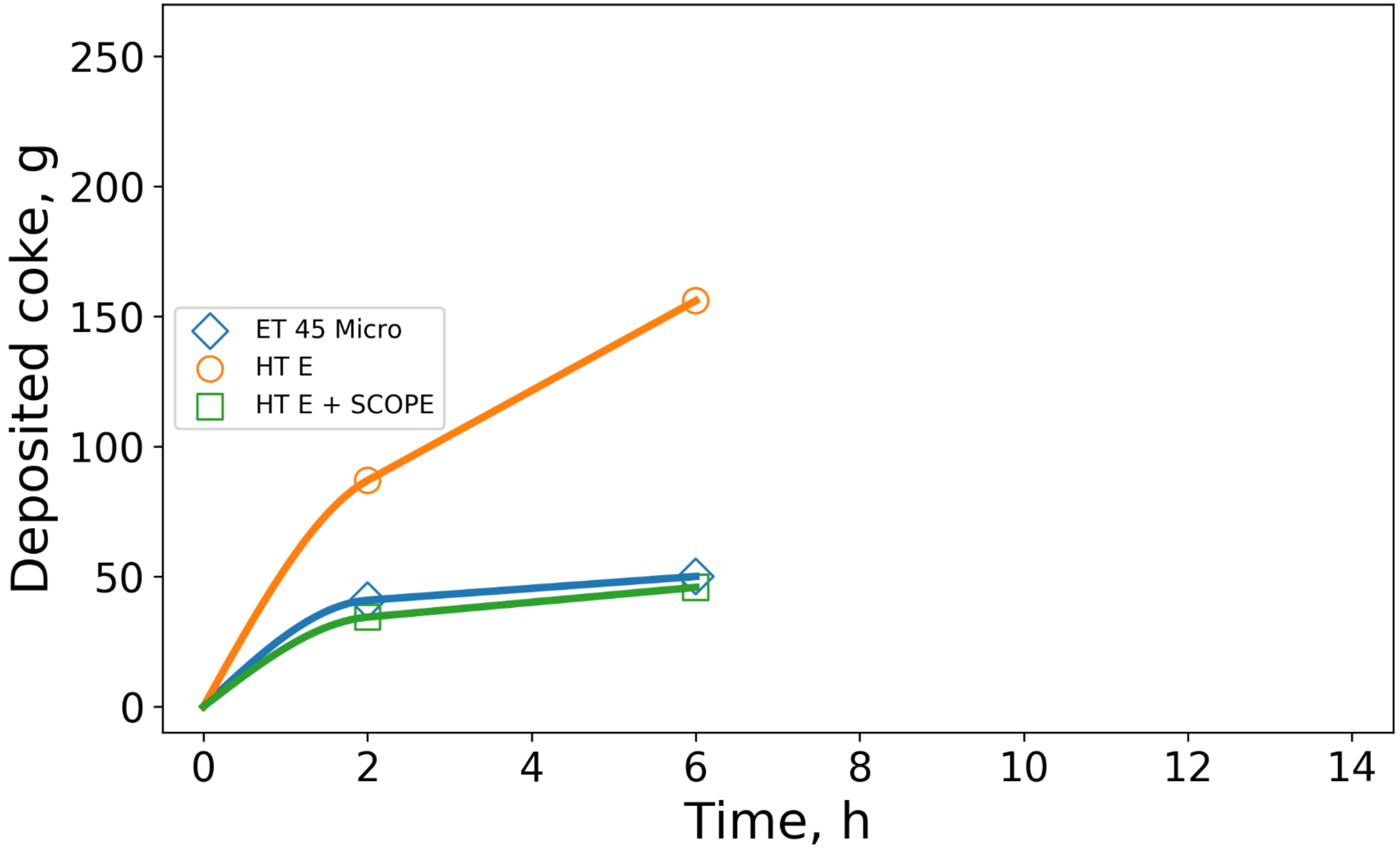
$\sim T_{refr}, T_{flue}$

$\sim \dot{m}_{fuel}$



Zhang, Y. et al., Incident Radiative Heat Flux Based Method for the Coupled Run Length Simulation of Steam Cracking Furnaces. Ind. Eng. Chem. Res. 2017, 56, 4156-4172.

Coke deposition



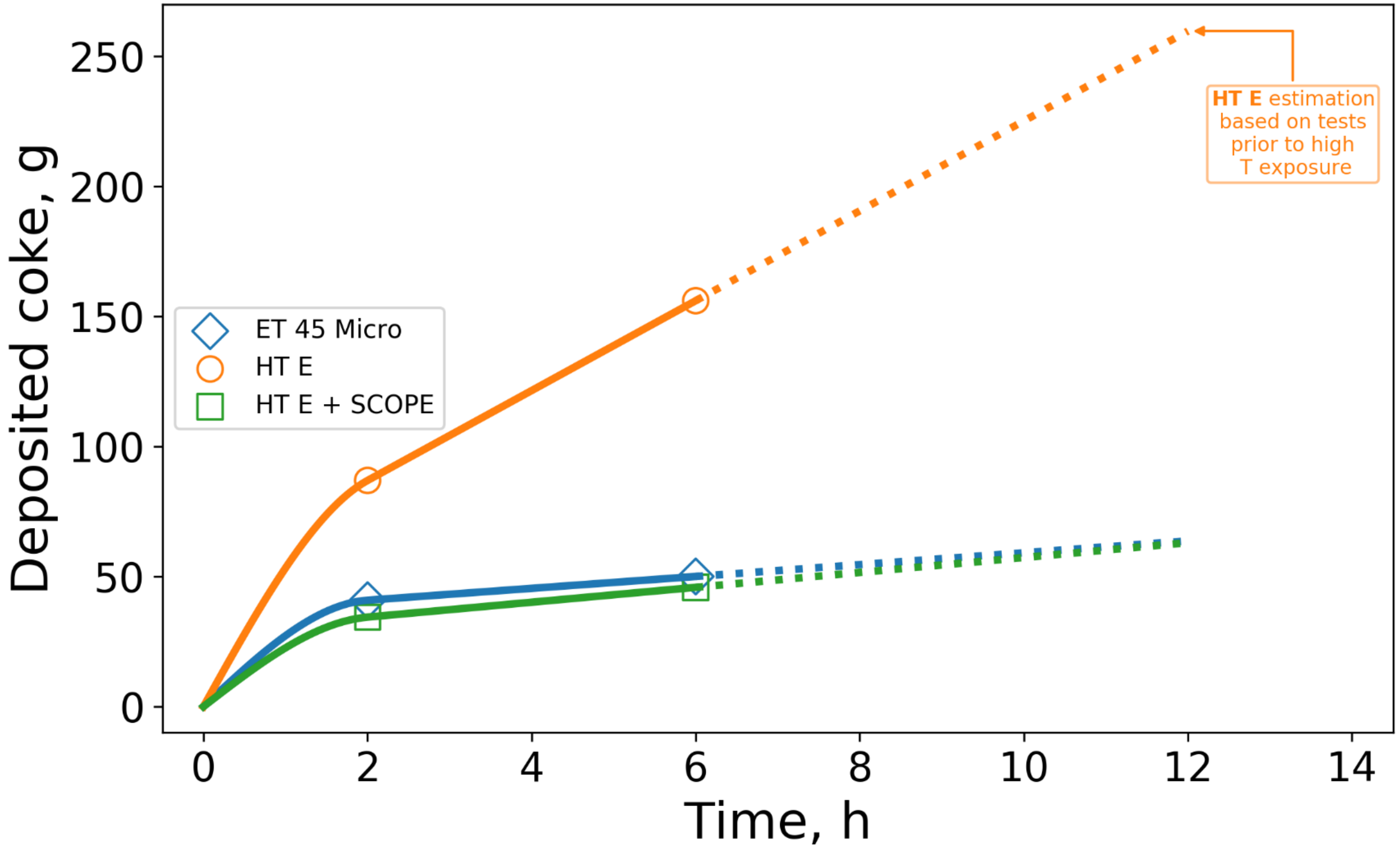
Coke after 2 (CC2) and 6h (CC3)

ET 45 Micro and HT E + SCOPE comparable

HT E significantly worse

Line: estimated coking curve

Coke deposition



Extrapolation for 12 h coke

Assumptions:

2 h (CC2) = Catalytic

6 h (CC3) = asymptotic

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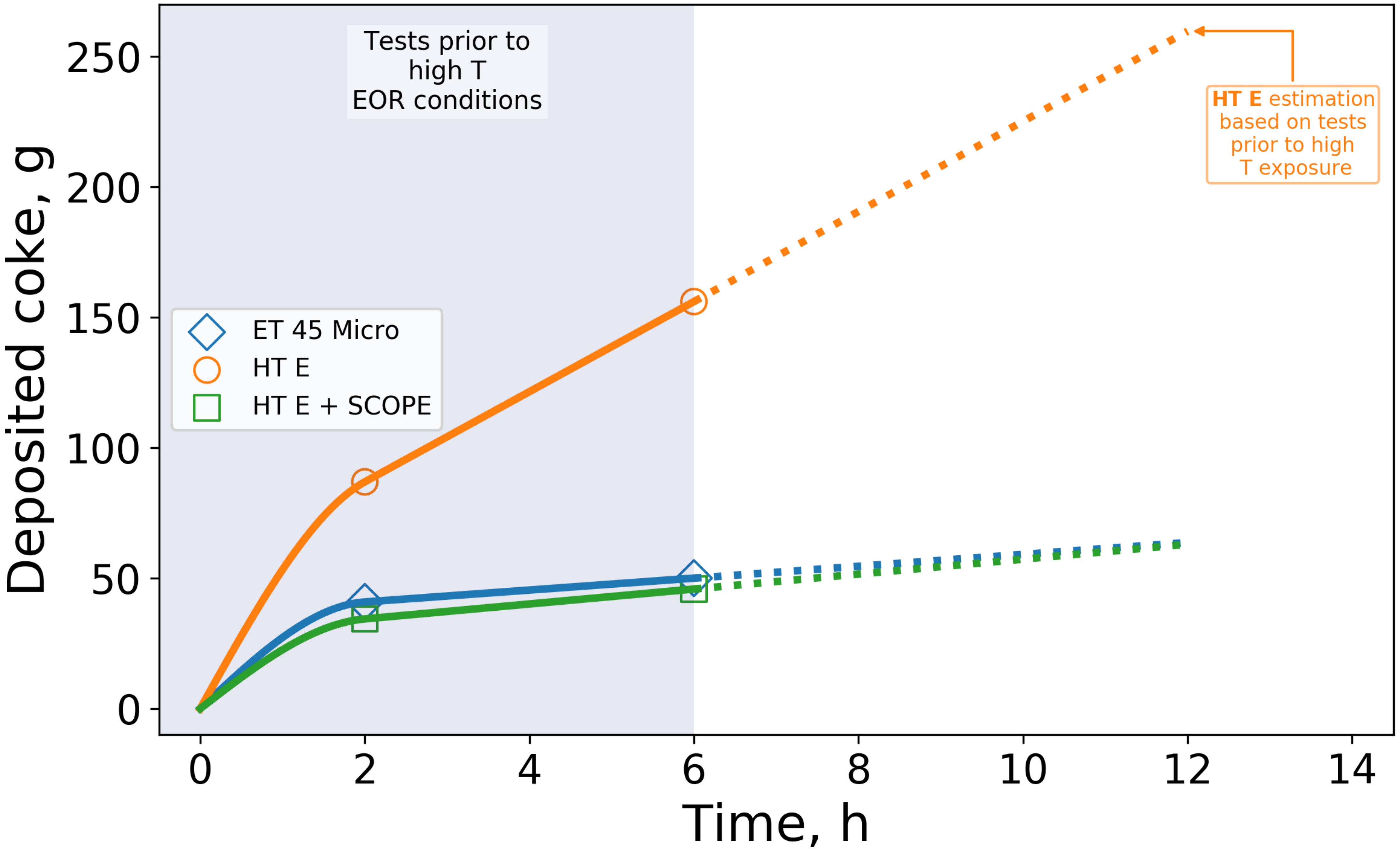
Coke deposition



Extrapolation based on tests prior to high T (EOR) exposure

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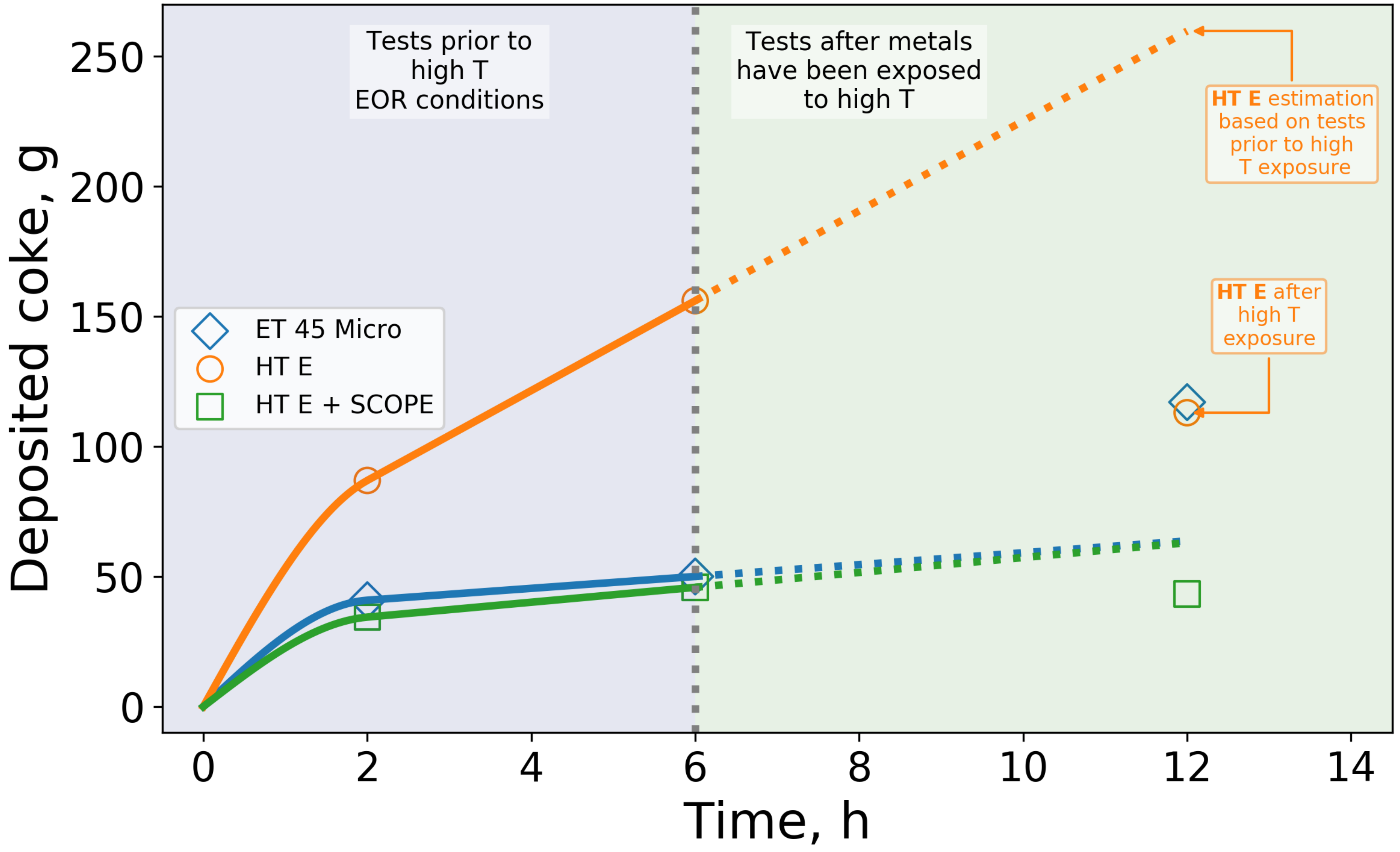
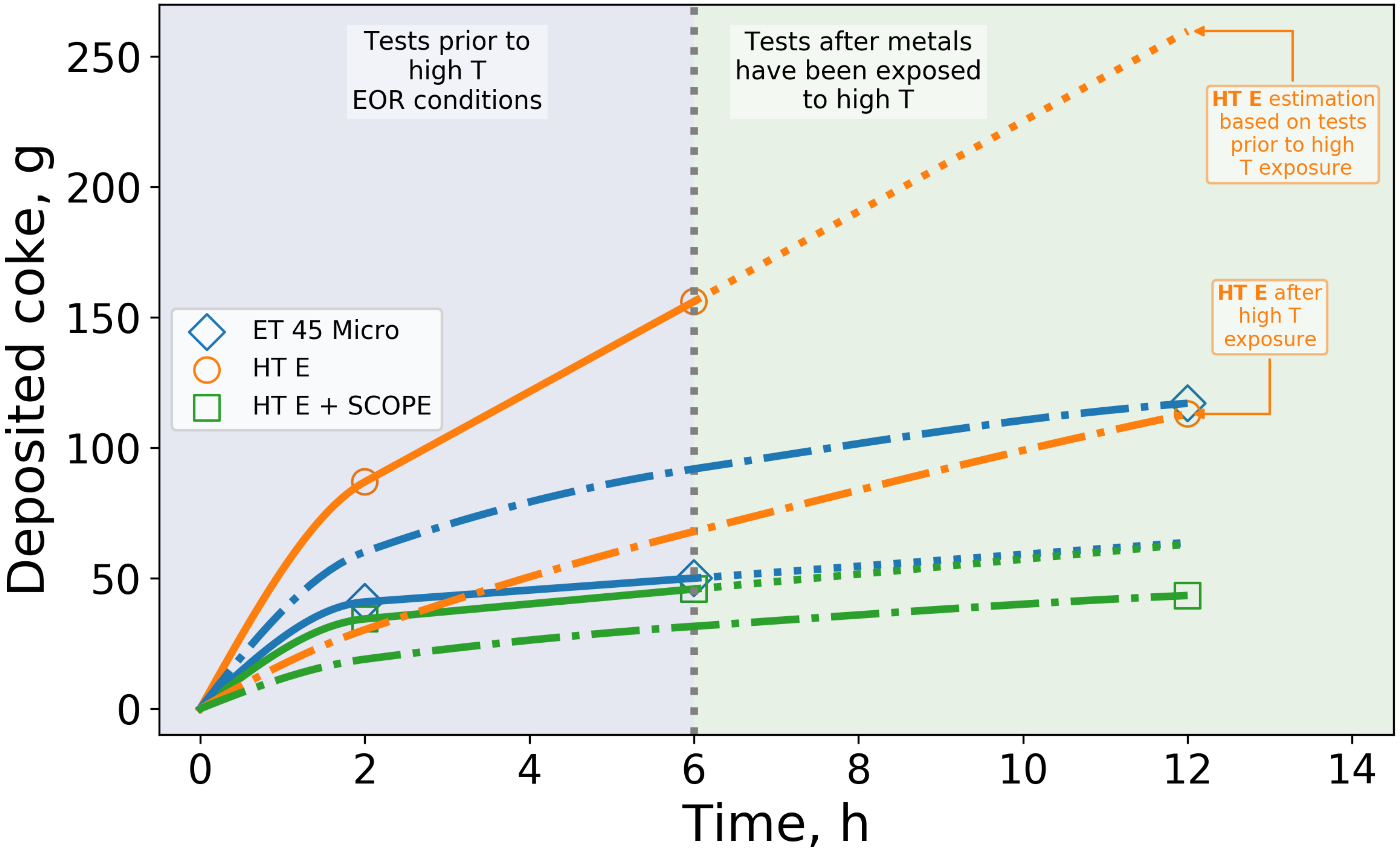
Coke deposition



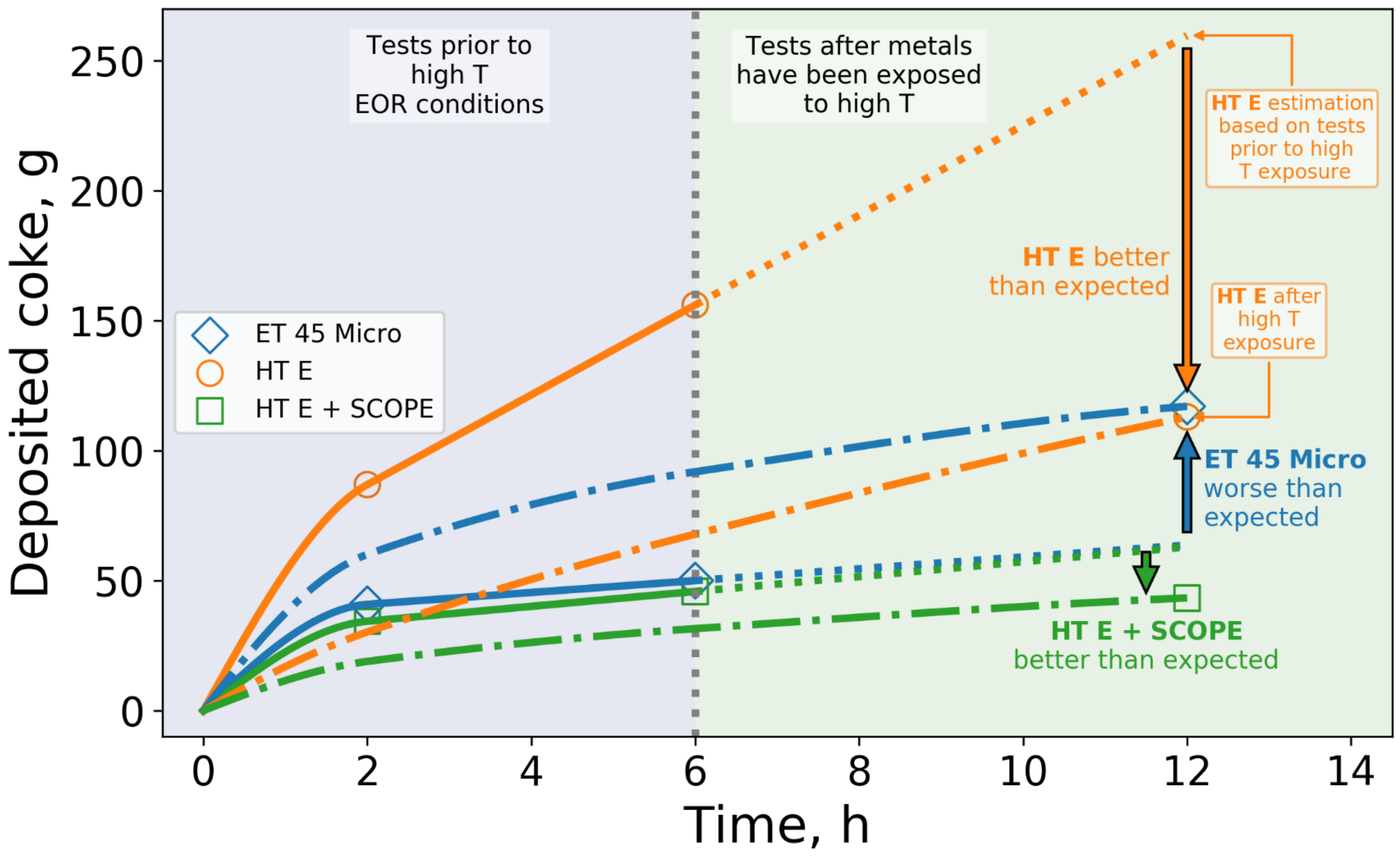
Coke after high T exposure

Coke deposition



Estimation coking curve

Coke deposition



HT E better than expected

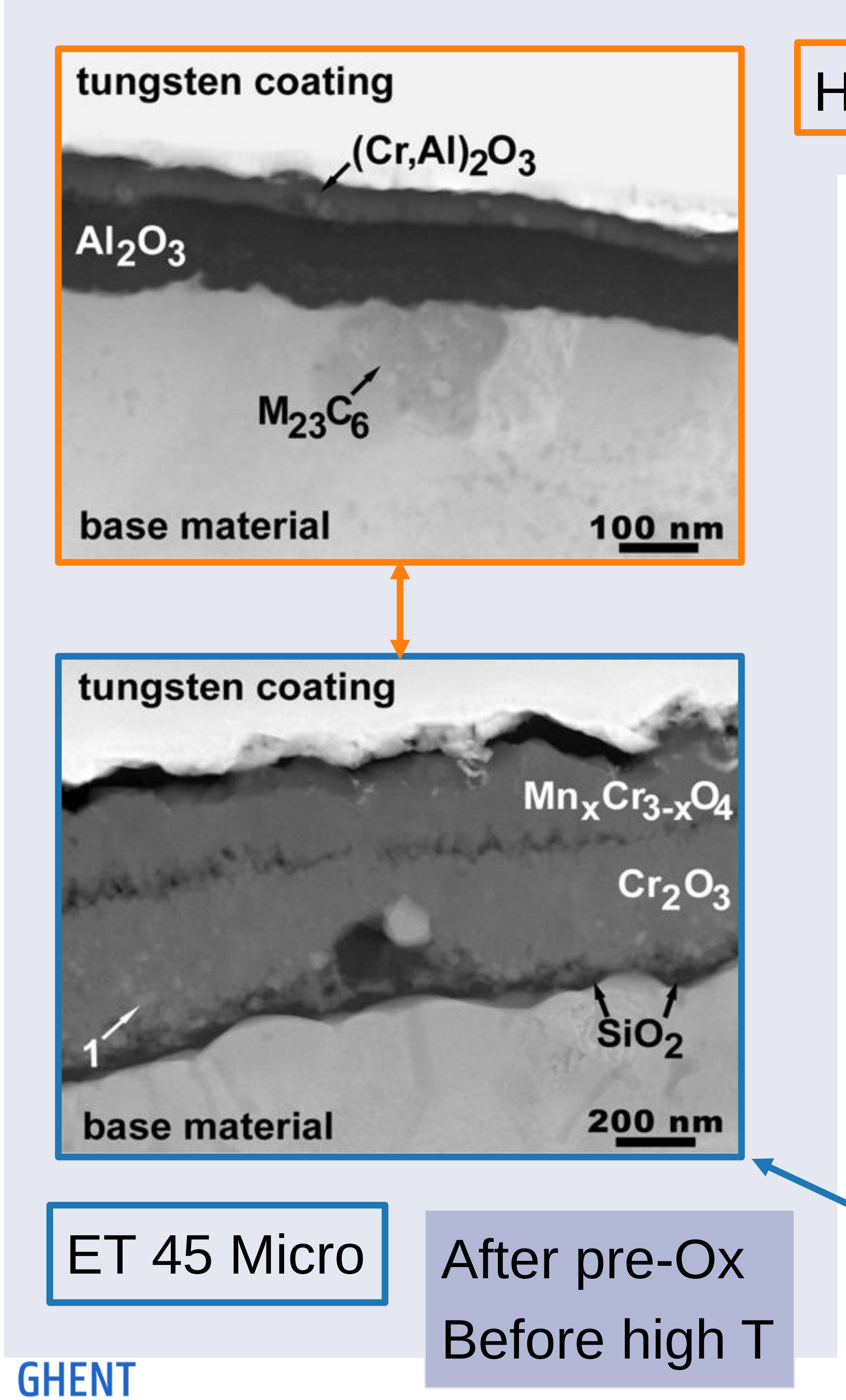
ET 45 Micro worse than expected

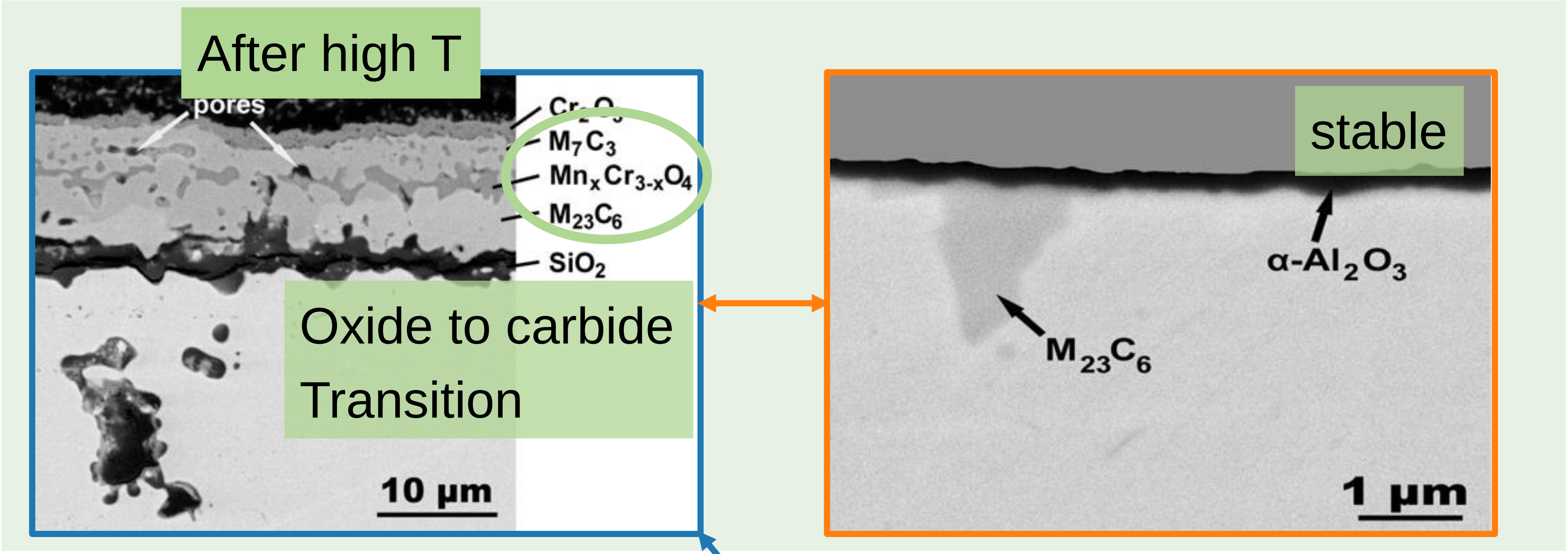
SCOPE design →

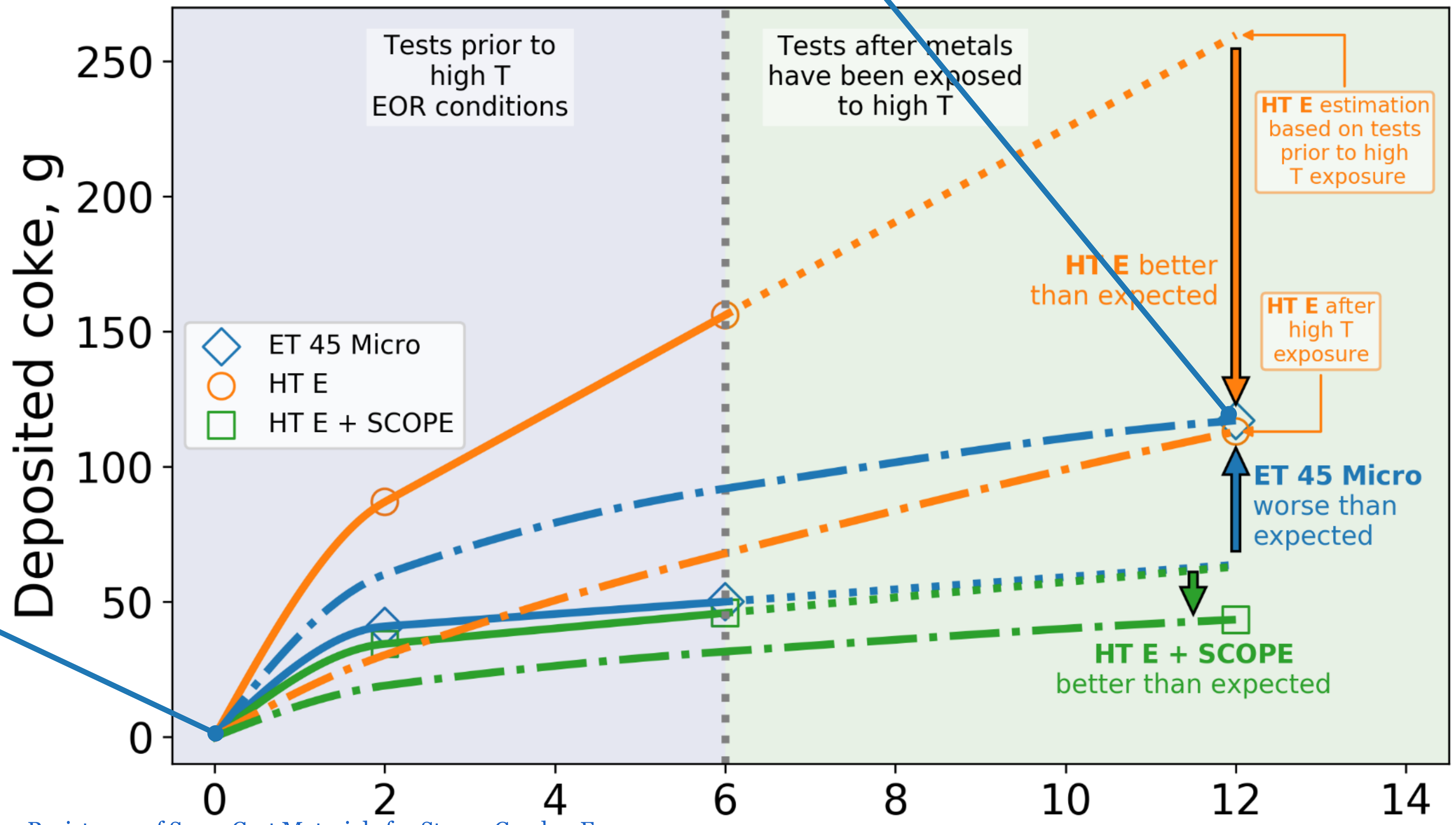
Lower temperatures

Lower influence high T excursion

Coke deposition







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Jakobi, et al., "The high-Temperature Corrosion Resistance of Spun-Cast Materials for Steam-Cracker Furnaces – A Comparative Study of Alumina- and Chromia-Forming Alloys", in NACE Corrosion, 2013.

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Conclusion

- After high Temperature (EOR) exposure HT E performs better, while the performance of ET 45 Micro drops
- ET 45 Micro → Oxide to carbide transition
- HT E → Formation stable α-Al_2O_3 scale
- Combining the advanced coil material (HT E) and novel 3D reactor design (SCOPE®) leads to
  - Increased run lengths
  - Improved product selectivities
  - Longer lifetime of the reactor coils
  - Higher energy efficiency of the furnace

Acknowledgments

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IMPROOF

Thank you for your attention!

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LCT DRIVING CHEMICAL TECHNOLOGY

LABORATORY FOR CHEMICAL TECHNOLOGY

Technologiepark 914, 9052 Ghent, Belgium

E info.lct@ugent.be
T 003293311757

https://www.lct.ugent.be

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GLOSSARY

Please add text