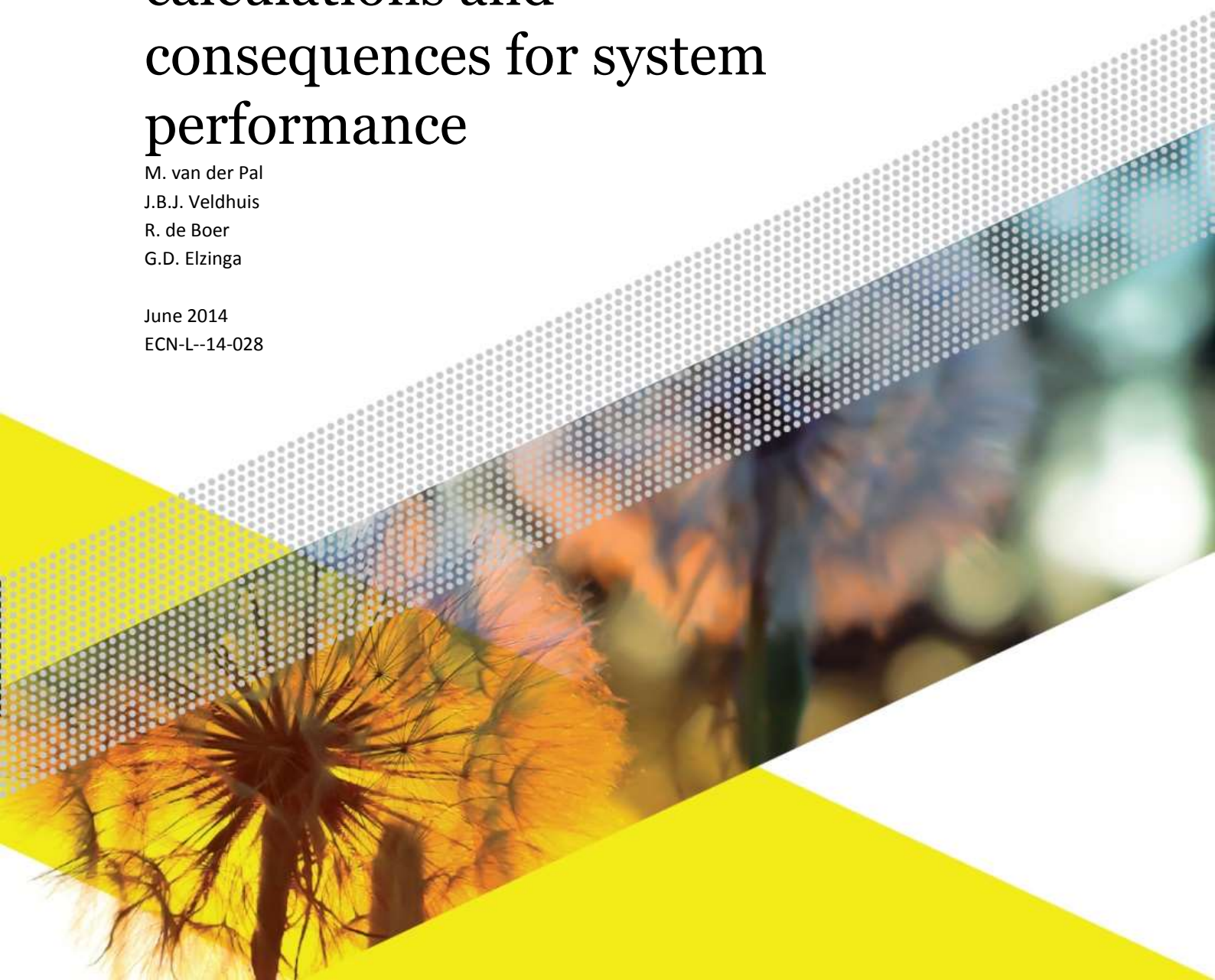


Composite materials for solid sorption heat pumps: measurements, model calculations and consequences for system performance

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- Introduction: experience from earlier work
- Composite materials: selection and preparation
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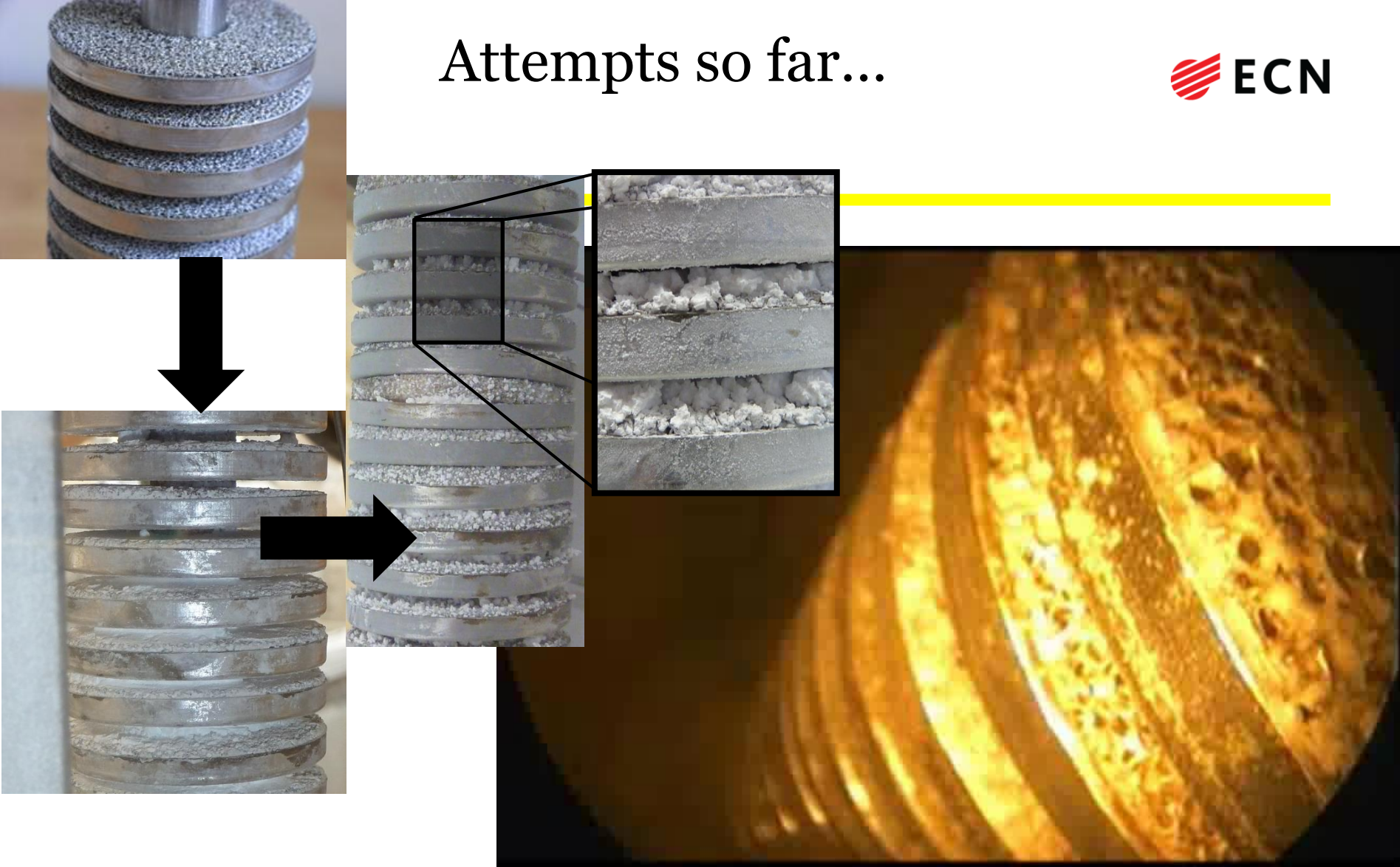
Introduction

- ECN is working on thermochemical heat transformers based on:
 - $\text{LiCl}(1-3)\text{NH}_3$ reaction in combination with $\text{MgCl}_2(2-6)\text{NH}_3$ for upgrading industrial waste heat to process heat
 - $\text{CaCl}_2(2-4-8)\text{NH}_3$ reaction in combination with $\text{MnCl}_2(2-6)\text{NH}_3$ and a compressor for upgrading low temperature waste heat to process heat
- Crucial for success of heat transformer:
 - Sufficient transfer(rate) of sorption heat to/from salt from/to Hex
 - Stable operation over many cycles

Why composite materials?

- Typical ammonia-salts properties are:
 - Poor thermal conductivity: only reasonable power density with thin layers = low COP
 - Poor strength: cannot create thick layers of salts with stable conditions
 - Volume changes: resulting in poorer connection with HEx
 - Tendency to become smaller and smaller crystals: loss of salt
- Composite materials can:
 - Improve thermal conductivity, resulting in shorter cycle times = higher power density
 - Provide structure for salts, including porosity and room to swell/shrink
 - Immobilise the salt

Attempts so far...



Composite selection and preparation

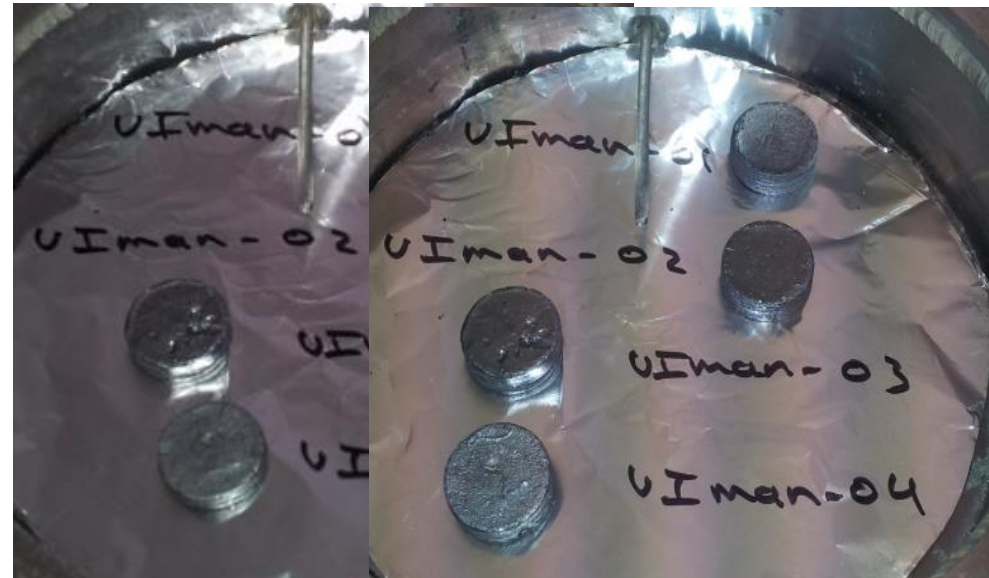
- Based on literature most promising material for salt-composite: ENG
- Preparation based on literature info
 - Method 1: mixing of ENG and salts followed by pressing to desired density
 - Method 2: pressing (or purchasing) ENG to desired density followed by impregnating with salt from solution

Results preparation

Solids mixing of ENG and salts



Impregnating ENG with salts



Analyses

- Thermal conductivity using Hotdisk thermal conductivity meter
- Cycle stability using micro flow reactor

Hotdisk measurement



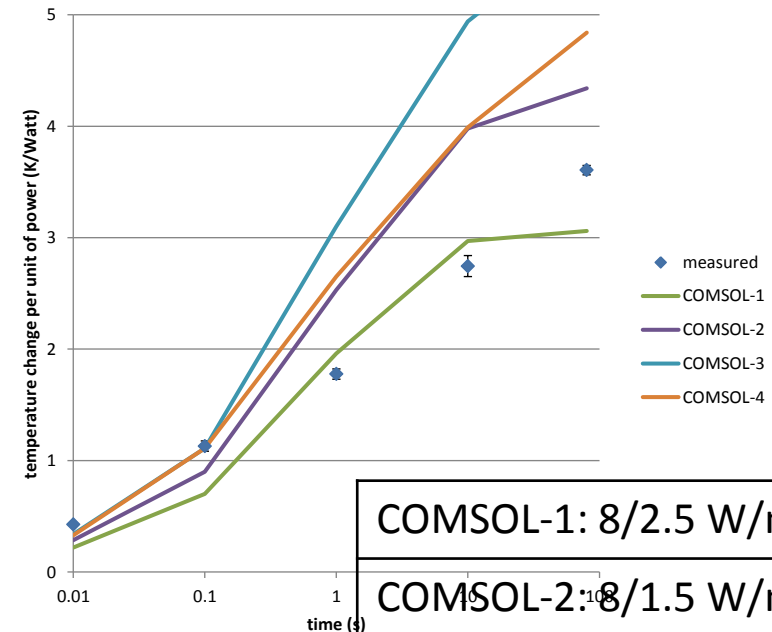
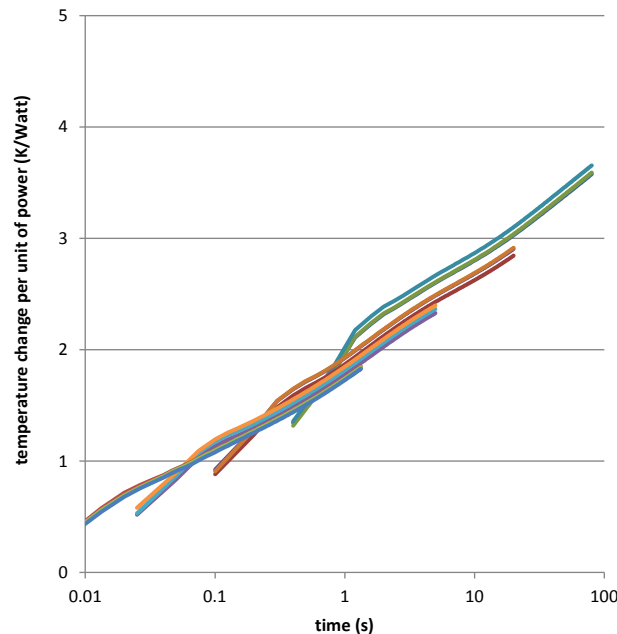
Principle:

- Transient plane method
- Constant heat flux provided by sensor for set period
- Simultaneous with heat flux: measurement of electrical resistance of sensor \rightarrow proportional to temperature

Hotdisk measurement

- Assumed:
 - $\lambda_{\text{radial}} \neq \lambda_{\text{axial}}$
 - Heat capacity = sum of heat capacity ENG and heat capacity CaCl_2
 - No heat flow at sides of the sample
 - Temperature top of the sample is equal to ambient
- Conditions:
 - Temperature increase measured in 1 to 80 seconds intervals with power input chosen for optimal temperature rise (too low = poor signal/noise ratio, too high = too many second-order effects)
 - ENG measured with and without CaCl_2
- Analysis:
 - Comparison with COMSOL model with various values for λ_{radial} and λ_{axial}

Hotdisk results for ENG-CaCl₂·xNH₃



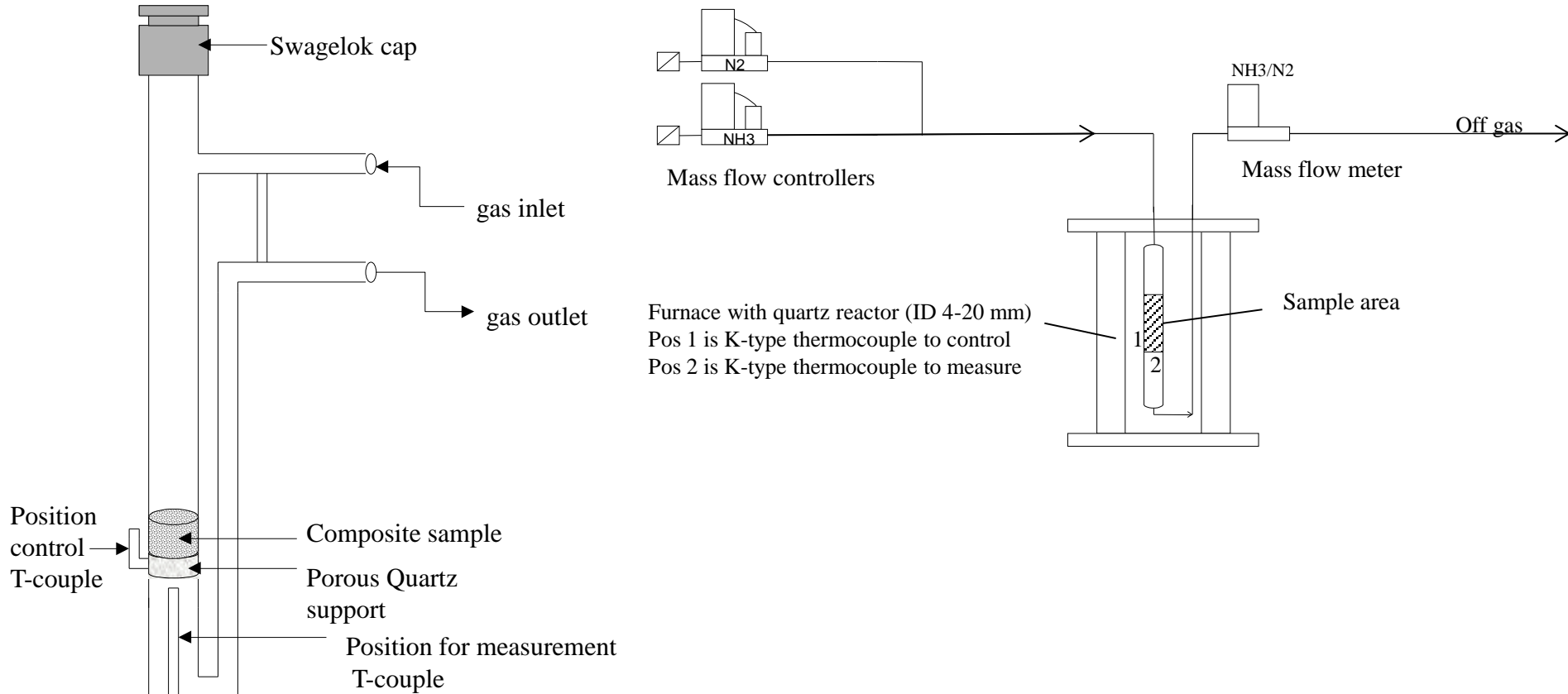
COMSOL-1: 8/2.5 W/mK

COMSOL-2: 8/1.5 W/mK

COMSOL-3: 8/1.0 W/mK

COMSOL-4: 16/1 W/mK

Setup: Micro flow reactor

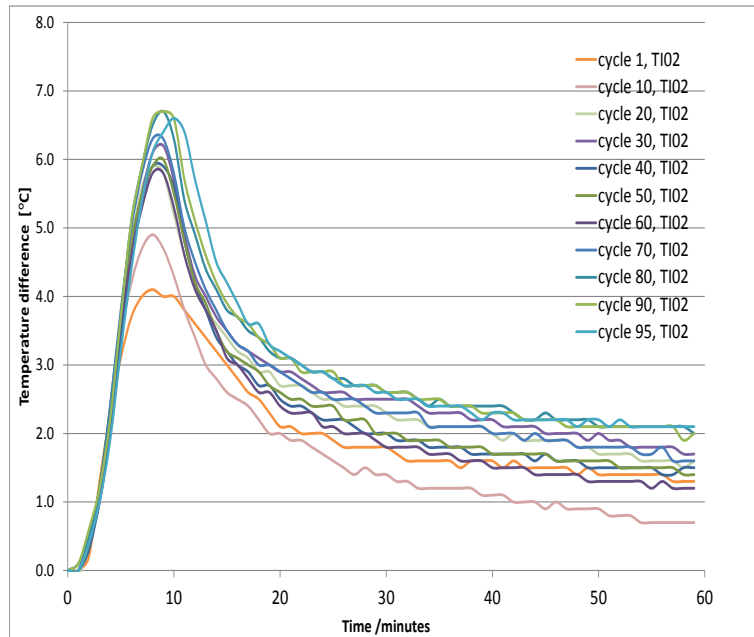


Micro flow reactor measurement

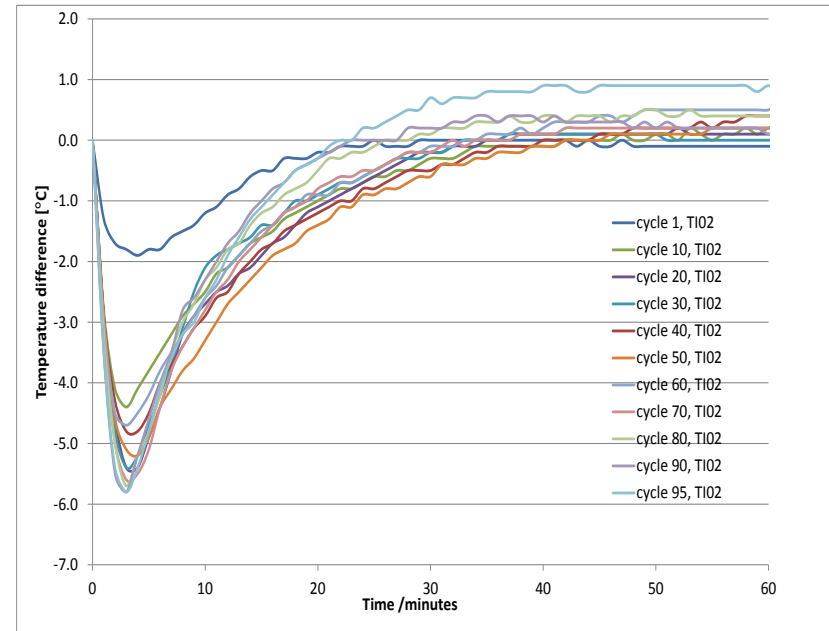
- Reactor and gas temperature set at constant value of 40°C
- Mass flow controller set at 10 ml/min
- Sample using ENG + CaCl₂
- Over 100 times: 1 hour NH₃ flow (adsorption), 1 hour N₂ flow (desorption)
- Measured parameters:
 - Flow out
 - Temperature composite
 - Temperature gas
- Visual inspection after 100+ cycles

Temperature profiles cycle tests

NH₃-flow (adsorption)

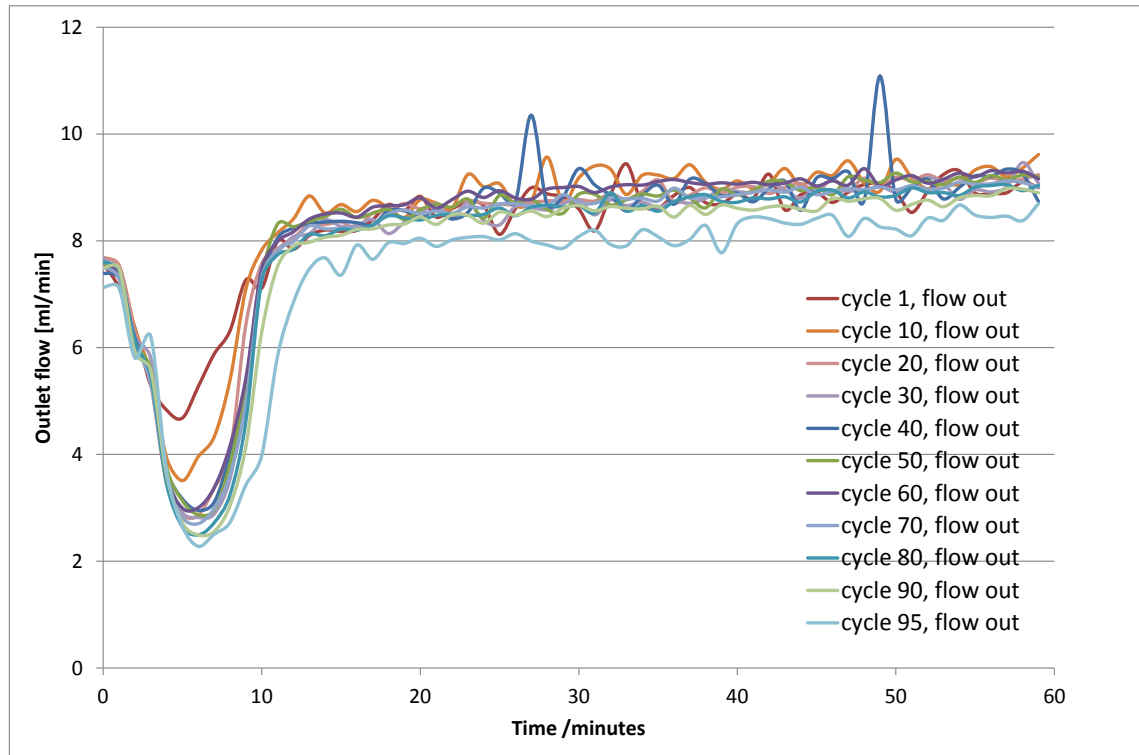


N₂-flow (desorption)

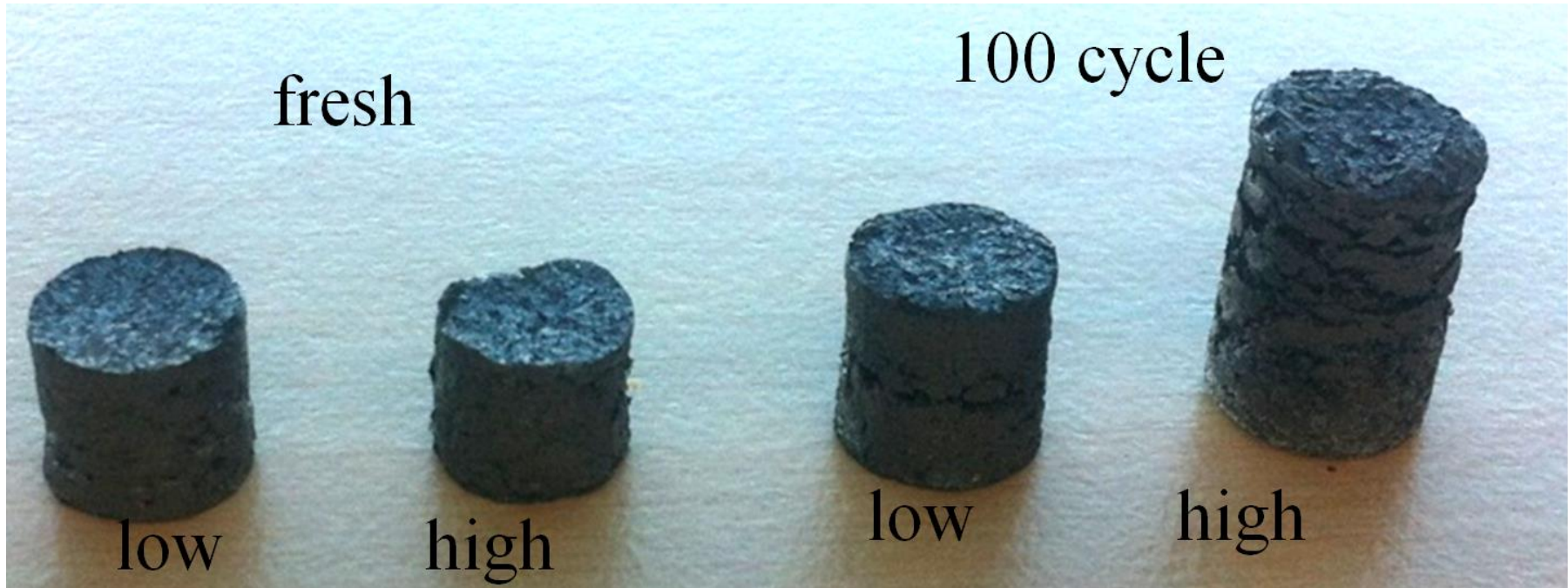


NH₃ flow out profiles cycle tests

NH₃-flow (adsorption)



Materials before and after 100+ cycles



Discussion and conclusions

- Hotdisk measurements:
 - Thermal conductivity of ENG+CaCl₂ seems very comparable with ENG properties
 - Assumed/unknown: do ENG and salt heat up at the same time?
 - COMSOL model calculations give good insight but less suited for quantifying thermal conductivity very precisely
- Microflow measurements:
 - Experimental method successful for determining composite stability regarding sorption behavior
 - Stable operation after first 10 cycles
 - Effect on material itself cannot be determined, visual inspection required
 - Setup allows for long-term testing of material (10,000+ cycles)



Questions?



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