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First Workshop ARENHA project: "Introduction to novel technologies related to ammonia-based energy storage"

Development of solid state ammonia absorption and storage

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2. Applications
3. How does it work?
4. Materials
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6. Model validation

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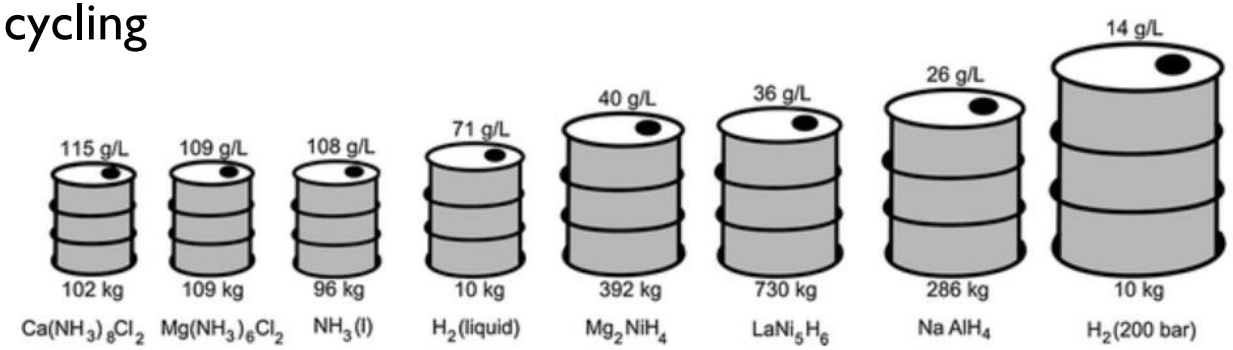
1. Solid state ammonia absorption and storage: Why's?

Solid metal salts can form stable metal ammines ($SrCl_2$, $MgCl_2$, $CaCl_2$, etc.)

- Partial pressure of ammonia at RT is low (2 mbar - 0.7 bar vs. 16 - 25 bar for liquid storage)
  - Solves safety issues for mobile applications
  - Enables low pressure ammonia synthesis
- Volumetric hydrogen density is high
- Stability over cycling



Volumetric hydrogen capacity by 8 hydrogen storage methods

Klerke et al., 2008

2. Solid state ammonia absorption and storage: Applications

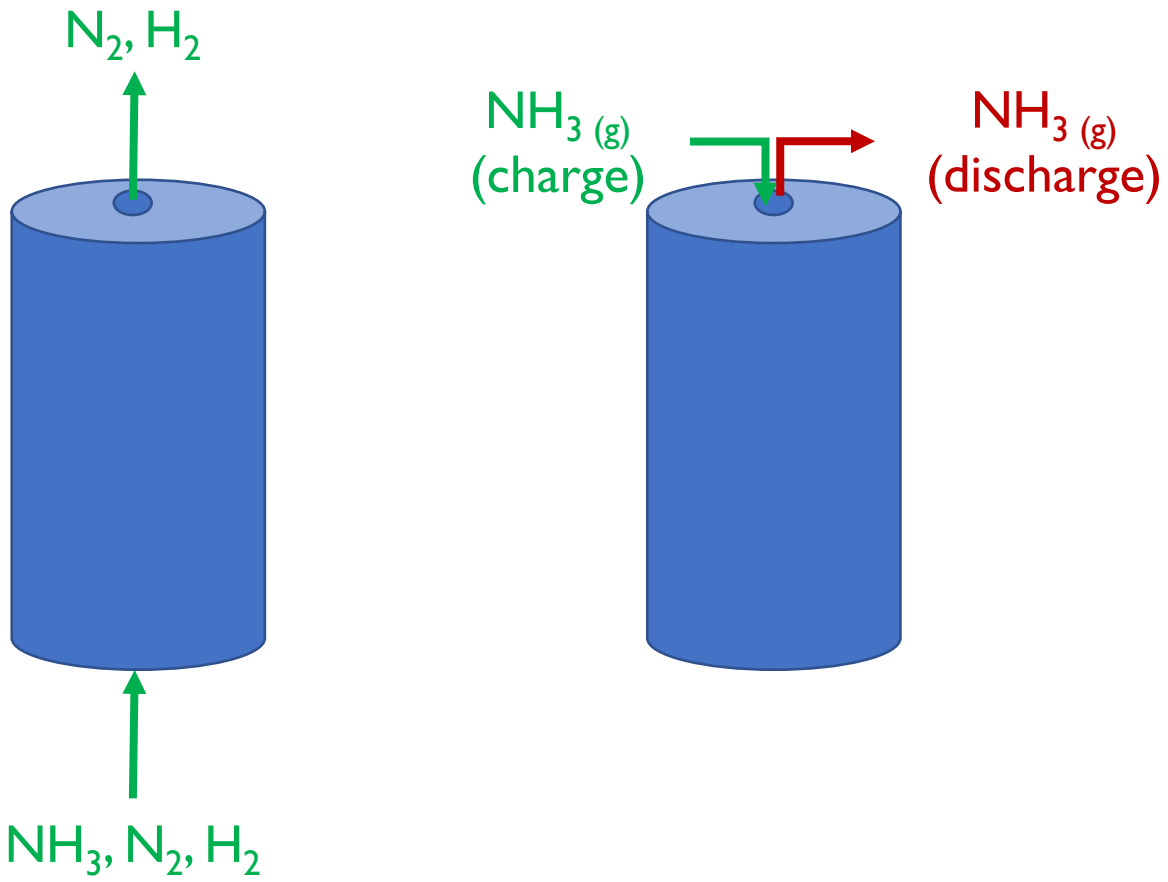
- Ammonia for hydrogen storage and transportation - ARENHA
- Ammonia for deNO$_x$ of diesel engines exhausts - AMMINEX
- Ammonia absorber for low pressure ammonia synthesis - AREHNA

DeNO$_x$ vessel from AMMINEX.
Capacity 3 kg$_{NH_3}$

3. Solid state ammonia absorption and storage: How does it work?

Ammonia absorber

Ammonia storage tank



Charge (absorption)

$$SrCl_2 + 8NH_3 \rightarrow Sr(NH_3)_8Cl_2 + Q$$

Discharge (desorption)

$$Sr(NH_3)_8Cl_2 + Q \rightarrow SrCl_2 + 8NH_3$$

4. Solid state ammonia absorption and storage: Materials

Desorption

$$Sr(NH_3)_8Cl_{2(s)} + Heat \leftrightarrow SrCl_{2(s)} + 8NH_{3(g)}$$

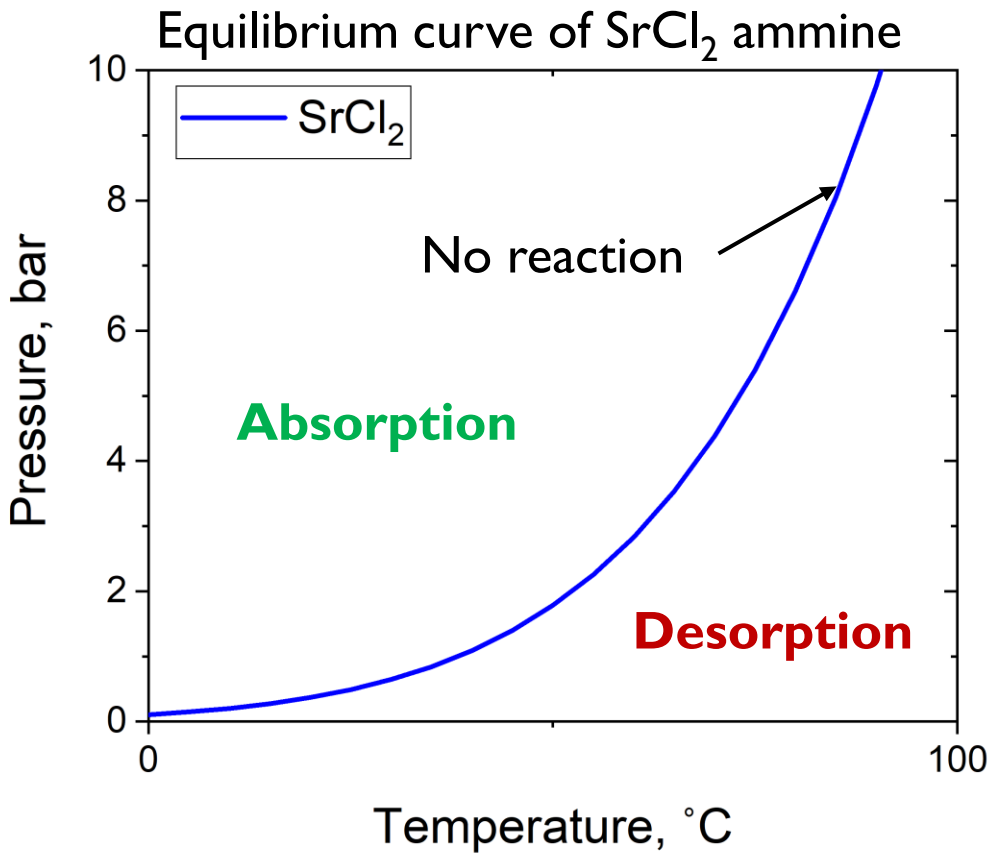
Absorption

Van't Hoff equation

$$p_{eq} = p_0 \cdot e^{-\frac{\Delta H}{RT}+\frac{\Delta S}{R}}$$

ΔH – enthalpy

ΔS - entropy



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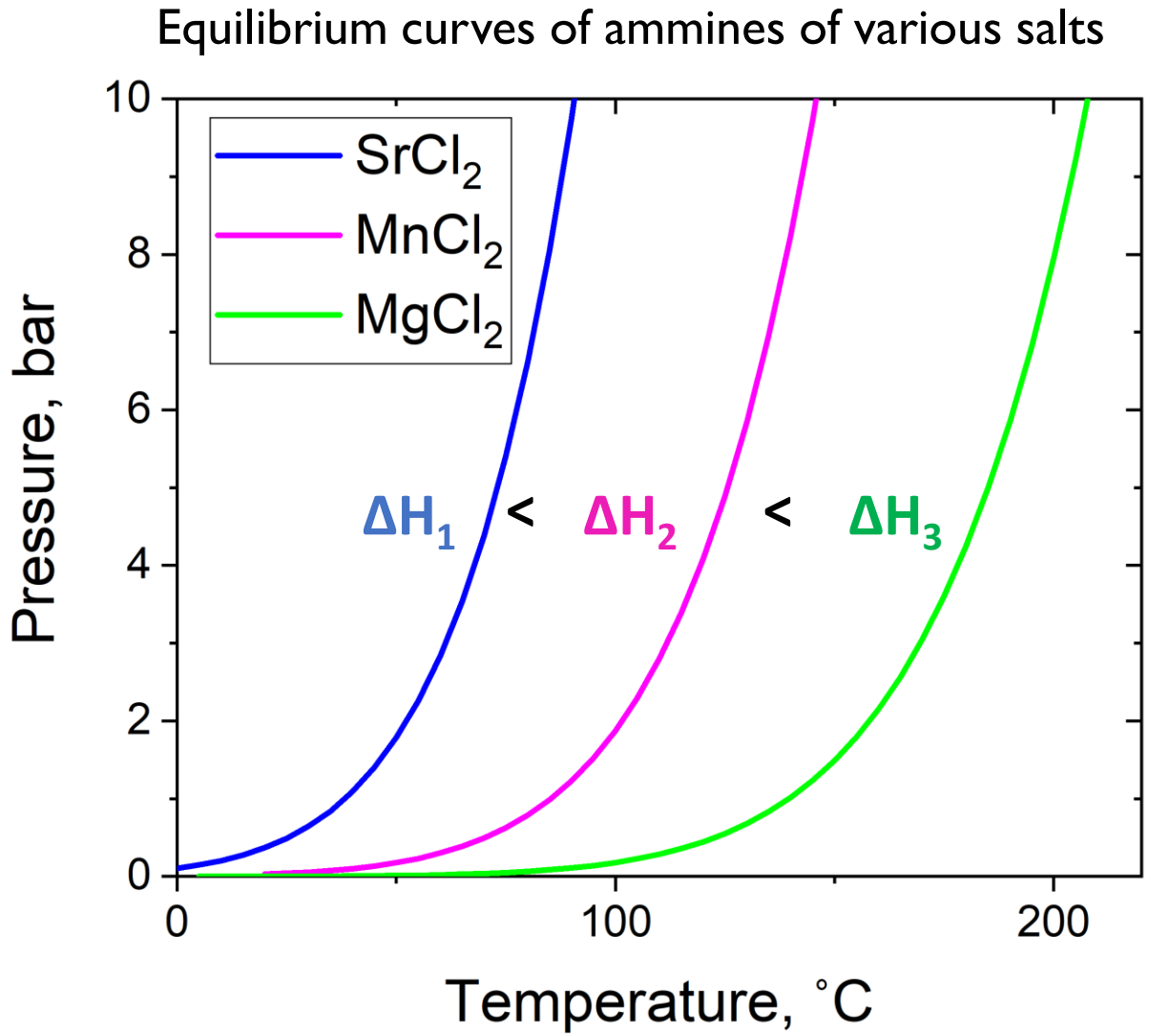
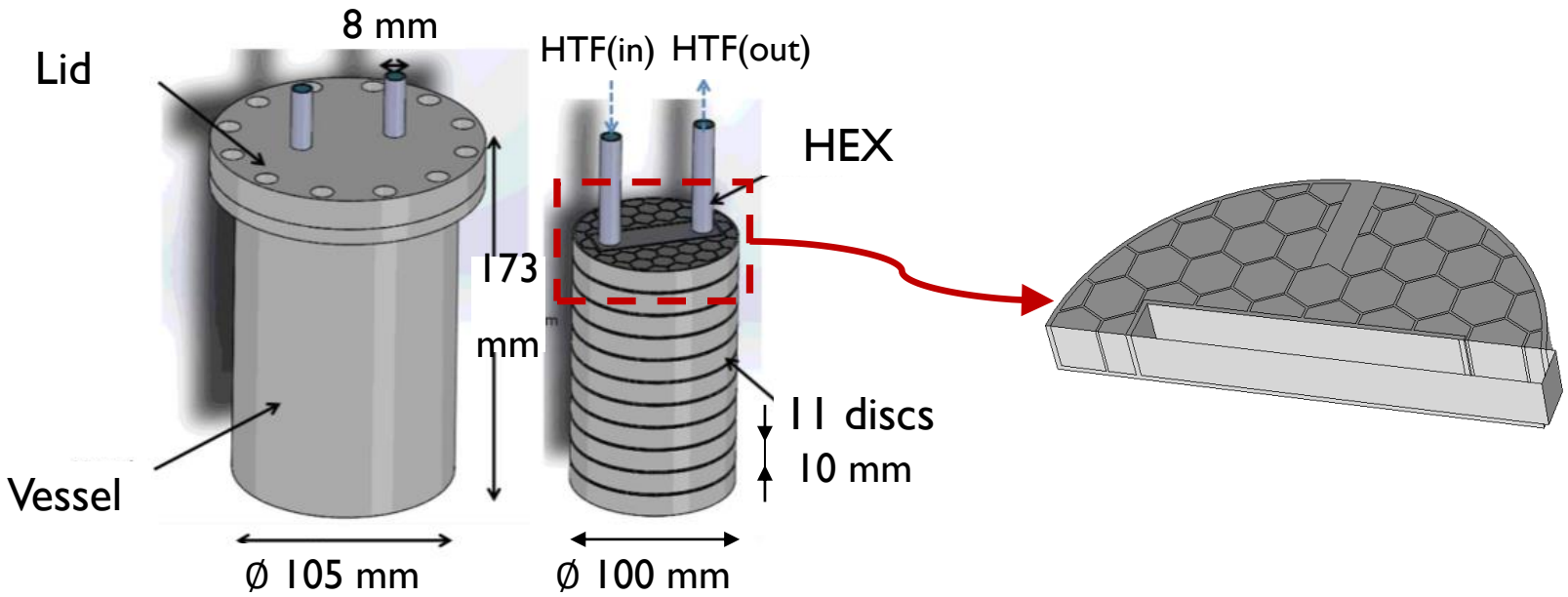
4. Solid state ammonia absorption and storage: Materials



5. Solid state ammonia storage tank: Modelling

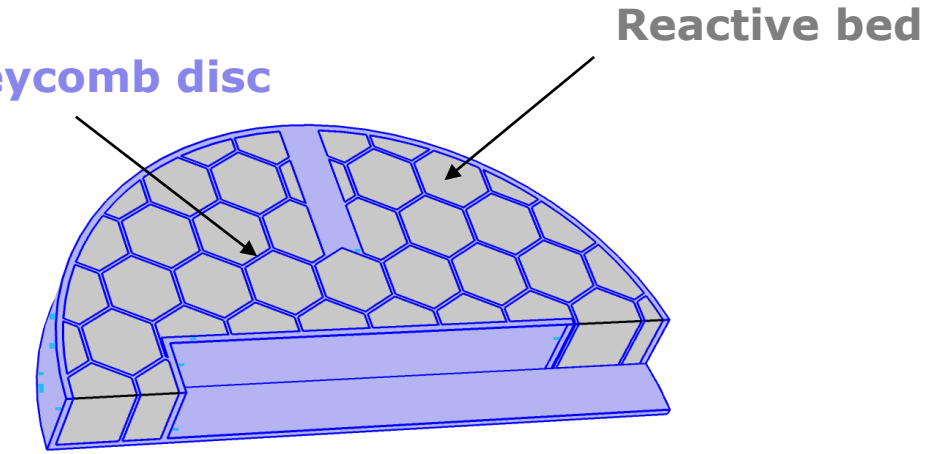
Goal: to develop an accurate numerical model of solid state ammonia storage tank

$$Sr(NH_3)_1Cl_2 + 7NH_3 \leftrightarrow Sr(NH_3)_8Cl_2 + Q$$



Soprani, 2016

5. Solid state ammonia storage tank: Modelling



Model: 3D, time-dependent

Software: COMSOL Multiphysics

Physics:

1. Mass transfer → pressure ***p*** and velocity ***u***
2. Reaction kinetics → reaction advancement *x*
3. Heat transfer → temperature *T*

Domains:

1. Honeycomb disc
2. Reactive bed (porous medium = salt + gas)
3. Gaseous ammonia

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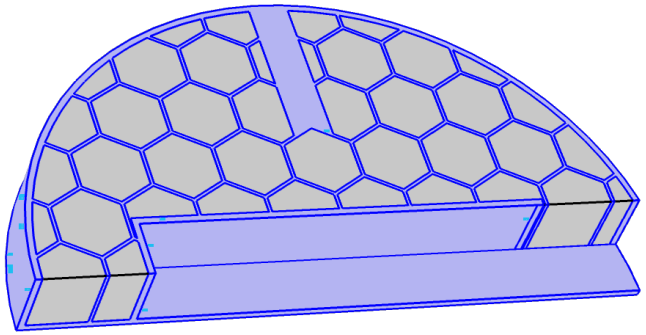
5. Solid state ammonia storage tank: Modelling



Physics:

1. ✓ Mass transfer → pressure ***p*** and velocity ***u***
2. ! Reaction kinetics → reaction advancement *x*
3. ✓ Heat transfer → temperature *T*

Required parameters:

1. Honeycomb disc: $\rho_{hd}, C_{p_{hd}}, k_{hd}$
2. Reactive bed: $\rho_{eff}, C_{p_{eff}}, k_{eff}, \varepsilon, \kappa$
3. Gaseous ammonia: $\rho_{NH_3}, C_{p_{NH_3}}, k_{NH_3}, \mu$

✓ From literature

✓ Easily calculated

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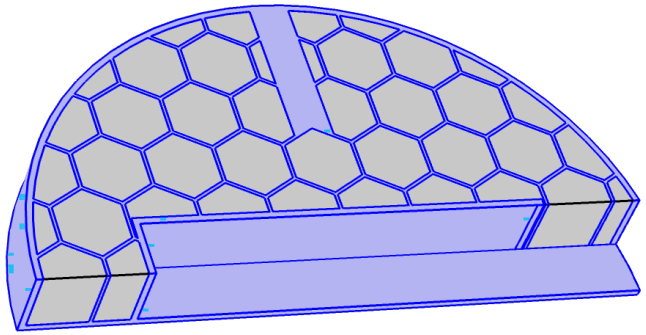
5. Solid state ammonia storage tank: Modelling



2. Reaction kinetics

$$\frac{dx}{dt} = k_0 e^{-\frac{E_a}{RT}} f(x) h(P)$$

$$x = \frac{SrCl_{2_{reacted}}}{SrCl_{2_{total}}}$$

Kinetic tetrad

- $T \rightarrow$ k_0 - pre-exponential factor
- $T \rightarrow$ E_a - activation energy
- $x \rightarrow$ $f(x)$ - reaction model function
- $p \rightarrow$ $h(p)$ – pressure impact function

5. Solid state ammonia storage tank: Modelling

1. **Y.Yuan et al.**, "Investigation of equilibrium and dynamic performance of SrCl2-expanded graphite composite in chemisorption refrigeration system," Appl.Therm. Eng., vol. 147, no. January 2018, pp. 52–60, 2019.

$m_{sorbent}$ = 210 g

2. **Huang et al.**, Modeling of gas-solid chemisorption in chemical heat pumps," Sep. Purif.Technol., vol. 34, no. 1–3, pp. 191–200, 2004.

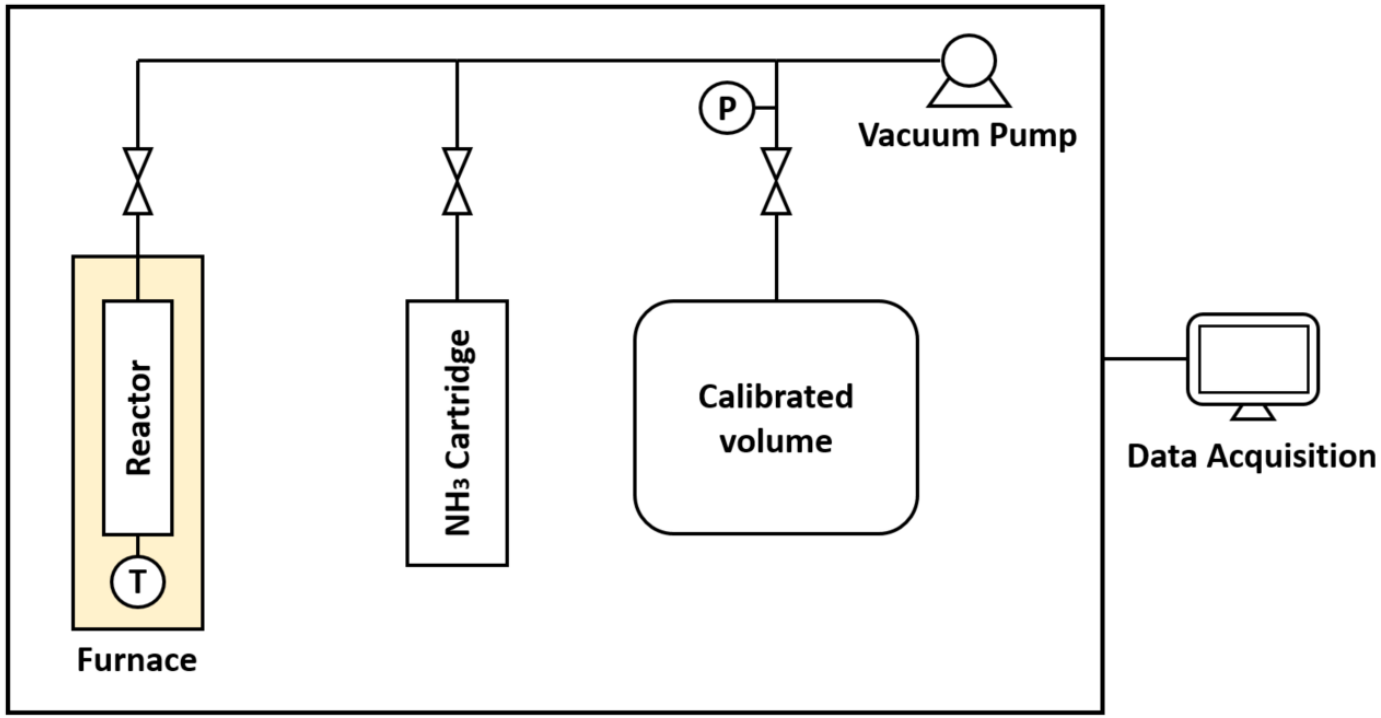
$m_{sorbent}$ = 2100 g

Large mass ➡ Effect of heat and mass transfer ➡ Apparent kinetics

Optimal mass ➡ No effect of heat and mass transfer ➡ Intrinsic kinetics

5. Solid state ammonia storage tank: Modelling

Barometric Sievert's type apparatus



$$\Delta p \rightarrow x$$

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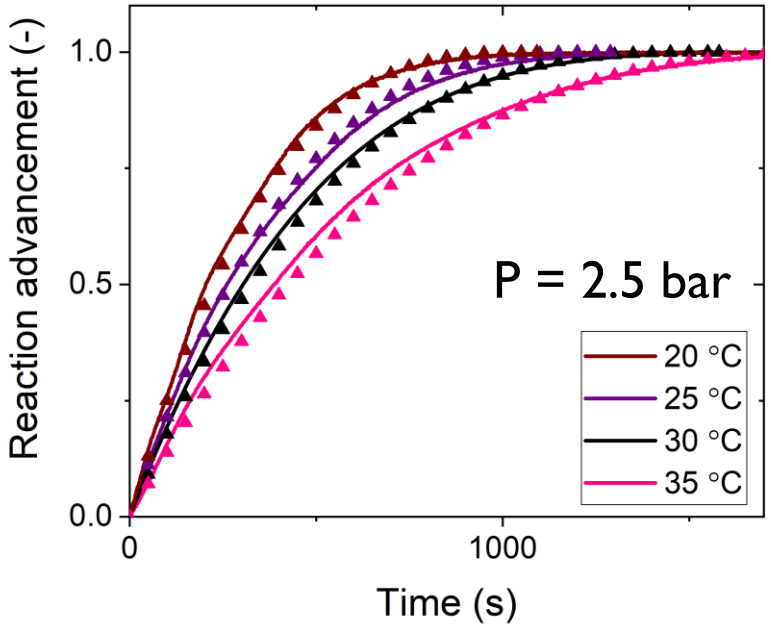
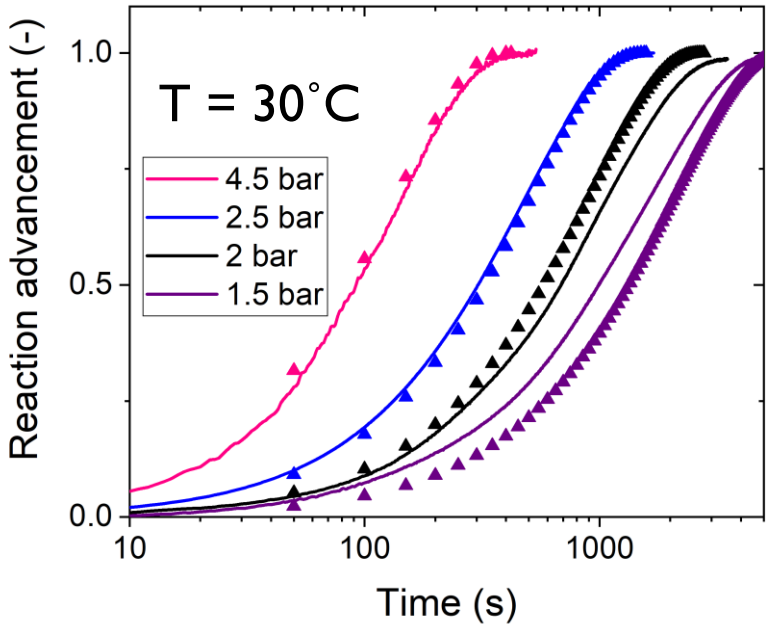
5. Solid state ammonia storage tank: Modelling

Reaction kinetics : Absorption

Mass - 71 mg

$$Sr(NH_3)_1Cl_2 + 7NH_3 \leftrightarrow Sr(NH_3)_8Cl_2 + Q$$





$$\frac{dx}{dt} = \boldsymbol{k_0} e^{-\frac{\boldsymbol{E_a}}{RT}} \cdot \boldsymbol{f(x)h(p)}$$

$$\boldsymbol{k_0} = 2.423 \times 10^7\ \mathrm{s^{-1}};\ \boldsymbol{E_a} = 66.1\ \mathrm{kJ\ mole^{-1}};$$

$$\boldsymbol{f(x)} = 3 \cdot (1 - \mathrm{x})^{\frac{2}{3}};\ \boldsymbol{h(p)} = \left(\frac{\mathrm{P} - \mathrm{P_{eq}}}{\mathrm{P_{eq}}}\right)^{1.8}$$

Karabanova et al., 2021

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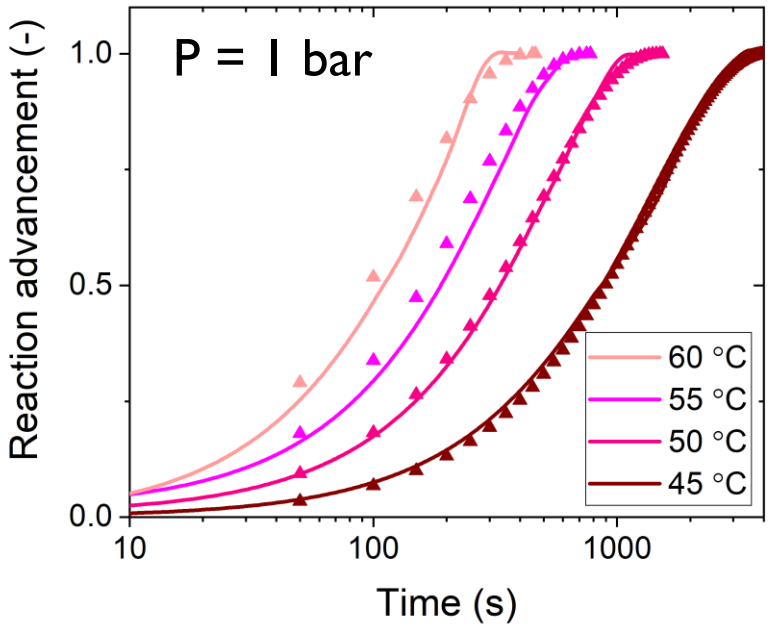
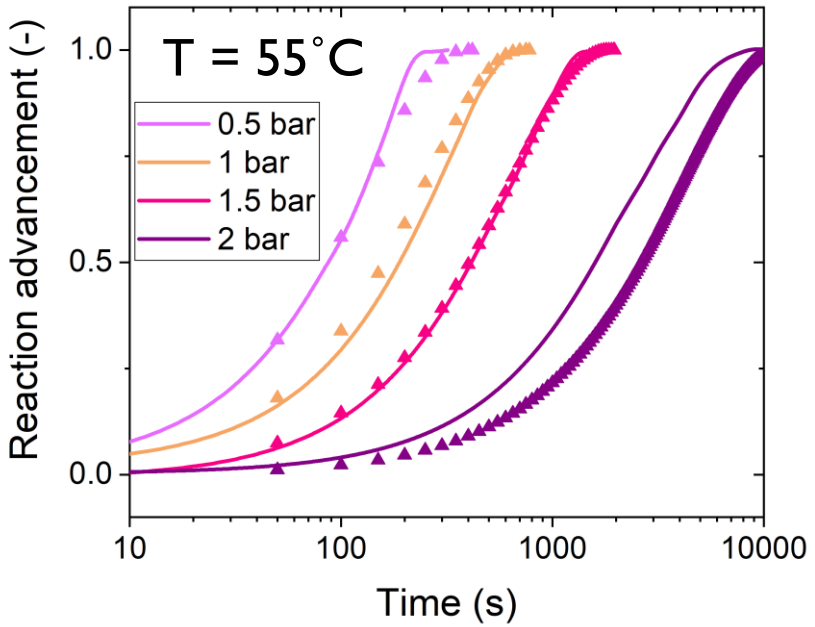
5. Solid state ammonia storage tank: Modelling

Reaction kinetics : Desorption

Mass - 71 mg

$$Sr(NH_3)_8Cl_2 + Q \leftrightarrow Sr(NH_3)_1Cl_2 + 7NH_3$$





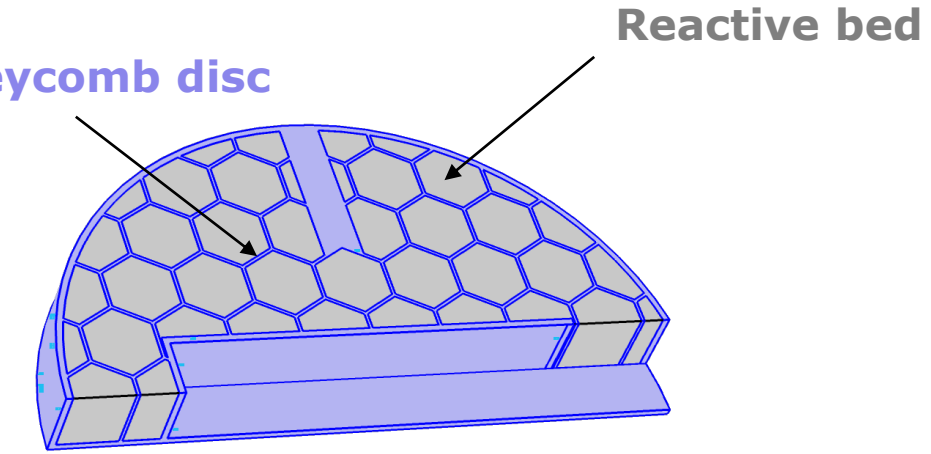
$$\frac{dx}{dt} = \boldsymbol{k_0} e^{-\frac{\boldsymbol{E_a}}{RT}} \cdot \boldsymbol{f(x)h(p)}$$

$$\boldsymbol{k_0} = 36754\ \mathrm{s}^{-1};\ \boldsymbol{E_a} = 43.9\ \mathrm{kJ\ mole}^{-1};$$

$$\boldsymbol{f(x)} = 3 \cdot (1-x)^{\frac{2}{3}};\ \boldsymbol{h(p)} = \left(\frac{\mathrm{P} - \mathrm{P_{eq}}}{\mathrm{P_{eq}}}\right)^{1.9}$$

Karabanova et al., 2021

5. Solid state ammonia storage tank: Modelling



Model: 3D, time-dependent

Software: COMSOL Multiphysics

Physics:

1. Mass transfer → pressure ***p*** and velocity ***u***
2. Reaction kinetics → reaction advancement *x*
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Domains:

1. Honeycomb disc
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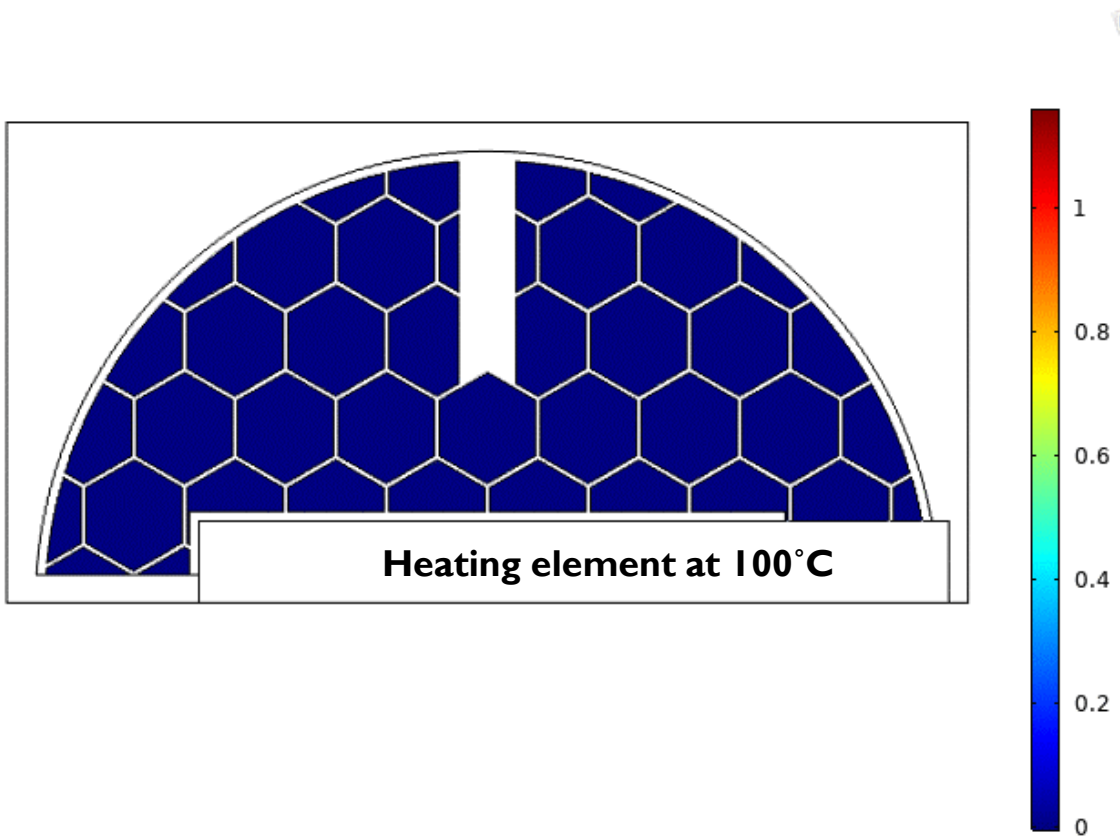
3. Gaseous ammonia

5. Solid state ammonia storage tank: Modelling

Modelled distribution of reaction advancement during desorption



Karabanova et al., 2021

6. Solid state ammonia storage tank: Model validation

We need: validated numerical model.

Validation methods:

1. Comparison to a reference solution

2. Experimental data:

Combination
- ➢ Local (thermocouple) → *T* at specific points
- ➢ Global (flowmeter) → global reaction advancement *x*

Our solution: Neutron Radiography

We can follow the state of the sorbent at **each point** of the storage tank

6. Solid state ammonia storage tank: Model validation

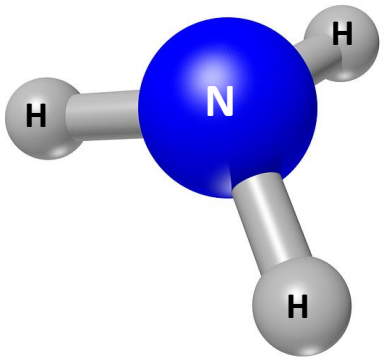
What is Neutron Radiography?

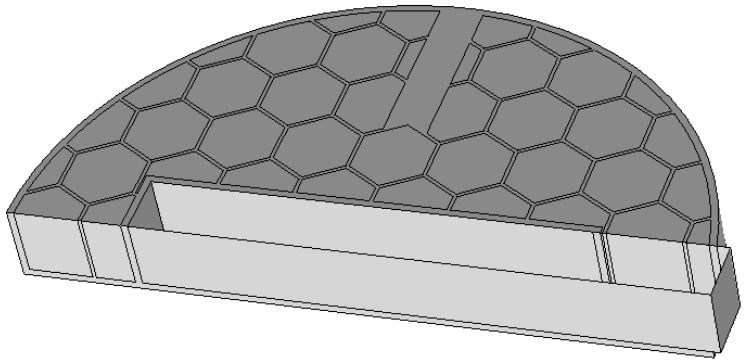
Similar to X-ray radiography

But X-rays ≠ Neutrons!

✓ Neutrons can ”see” hydrogen and hence ammonia

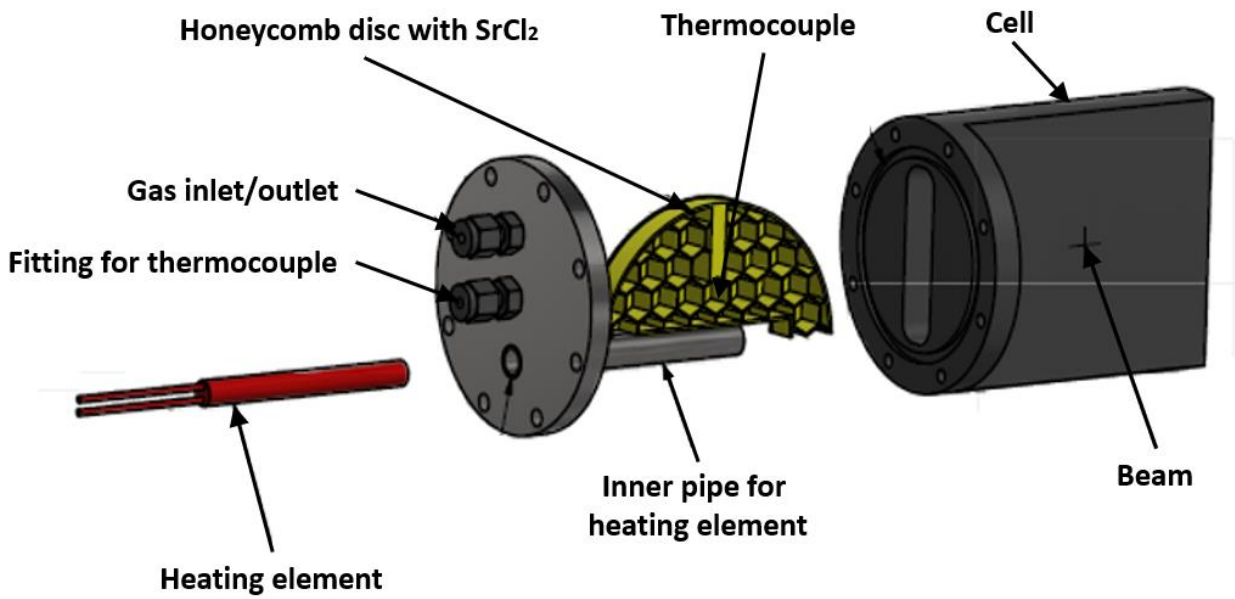
✓ High penetration power



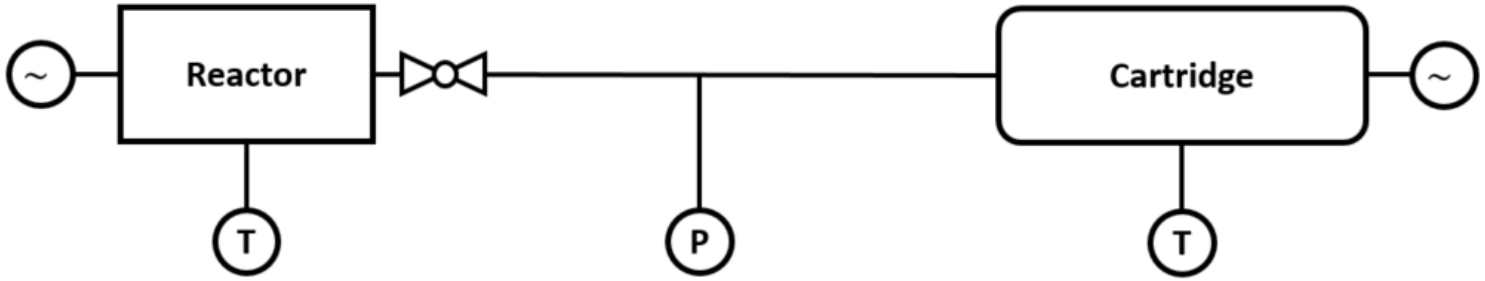


6. Solid state ammonia storage tank: Model validation

Reactor



Setup



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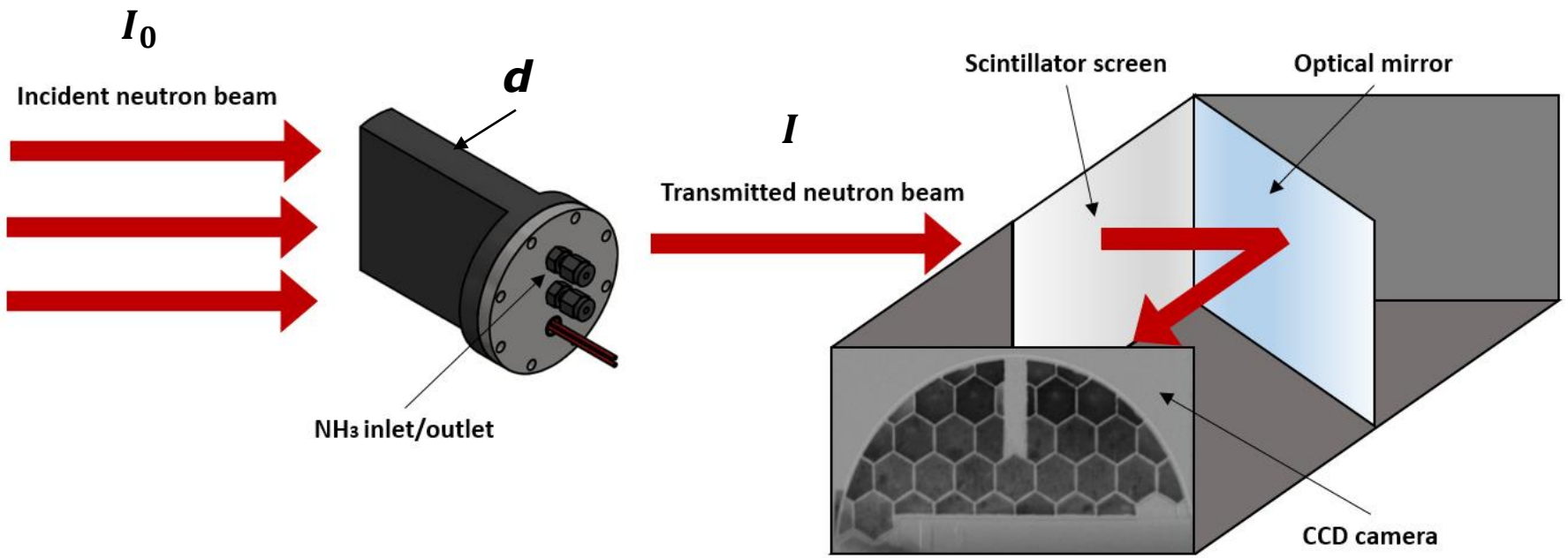
6. Solid state ammonia storage tank: Model validation



The Beer-Lambert's law

$$I = I_0 \cdot e^{-d \cdot \mu}$$

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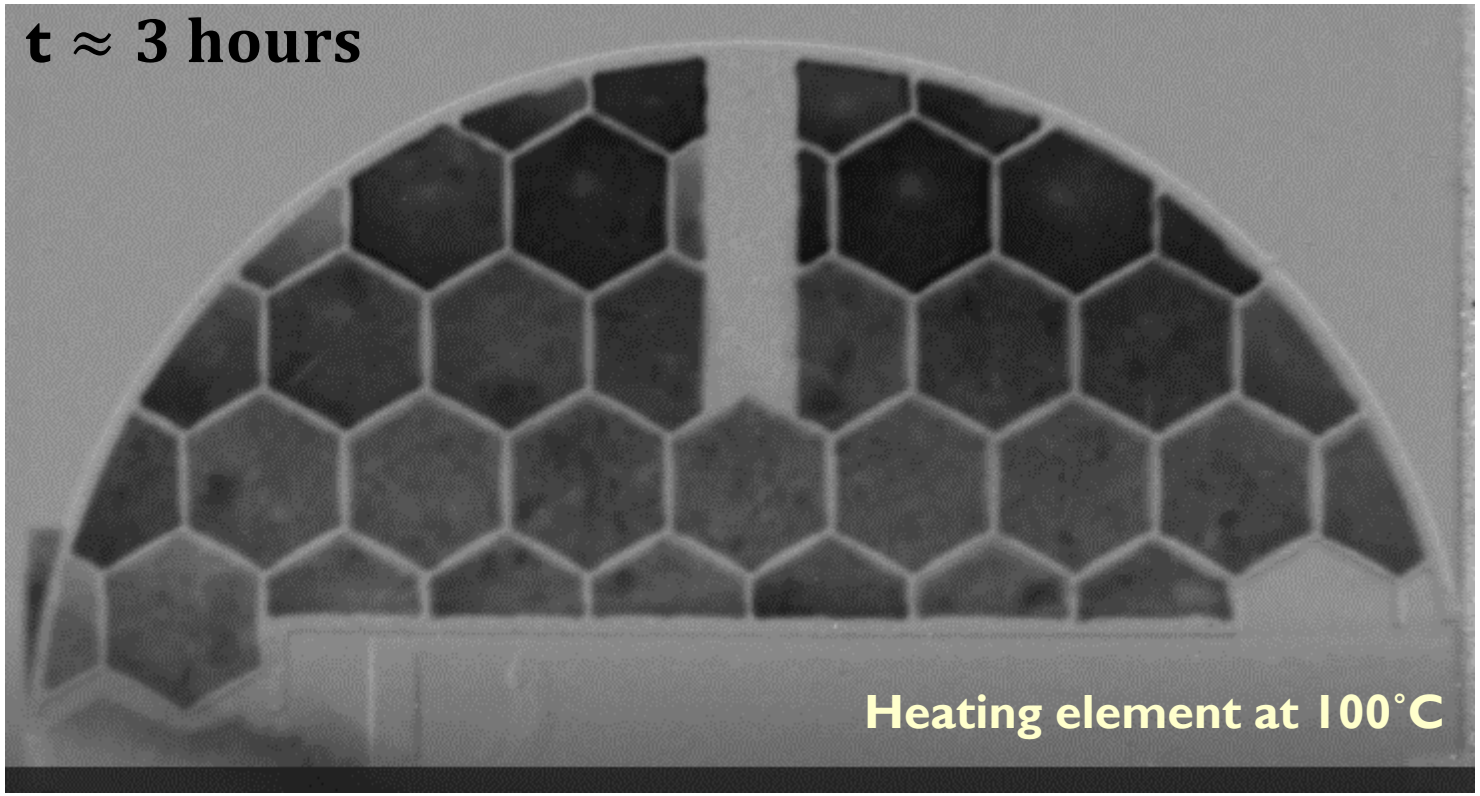
6. Solid state ammonia storage tank: Model validation

$$Sr(NH_3)_8Cl_2 + Q \leftrightarrow Sr(NH_3)_1Cl_2 + 7NH_3$$

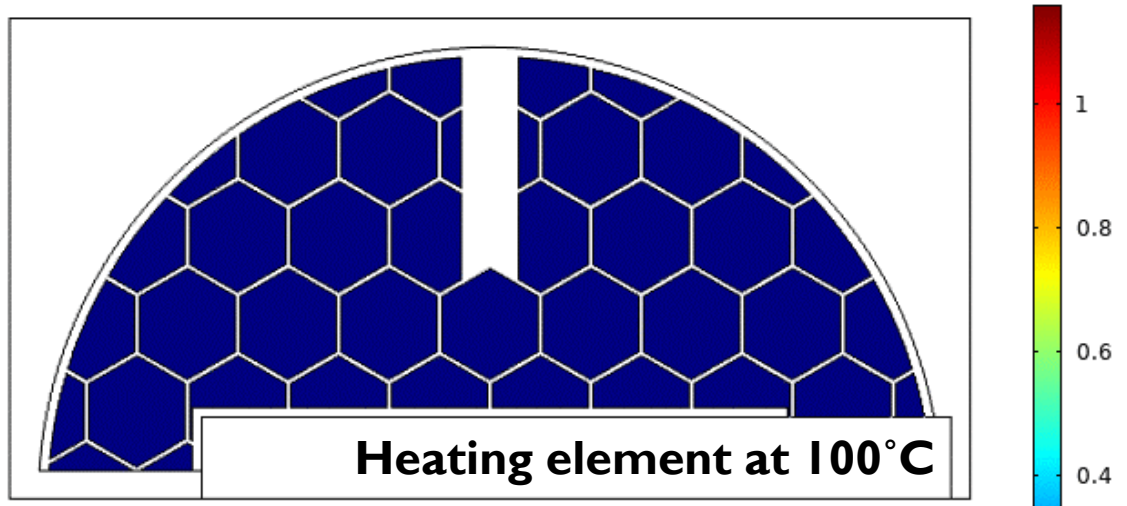
P ≈ 1 bar



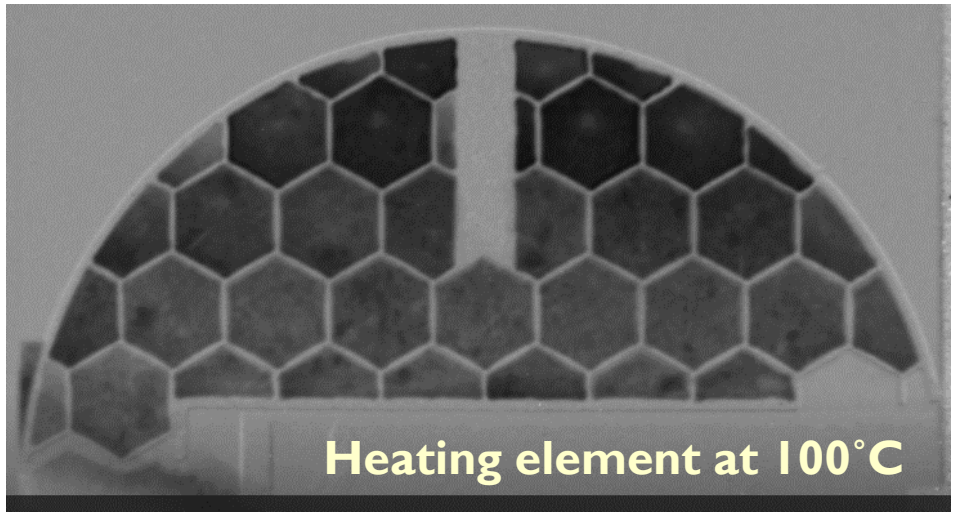
Karabanova et al., 2021

6. Solid state ammonia storage tank: Model validation

Model



Radiograhy



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Summary

1. Solid metal salts can form stable metal ammines ($SrCl_2$, $MgCl_2$, $CaCl_2$, etc.).

2. Systems with metal ammines can be used as solid state ammonia storage tank, $deNO_x$ vessels, as well as absorber for low pressure Haber Bosch process.

3. Knowledge model of storage tank shown in this presentation can be used for any geometries, materials, and applications.

4. Neutron radiography is a powerful tool to validate numerical models of ammonia-based systems.

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Development of solid state ammonia absorption and storage

First Workshop ARENHA project, ENGIE Lab CRIGEN, 07-04-2022

Thank you for your attention

Website project: https://arenha.eu/

Contact: anaka@dtu.dk

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