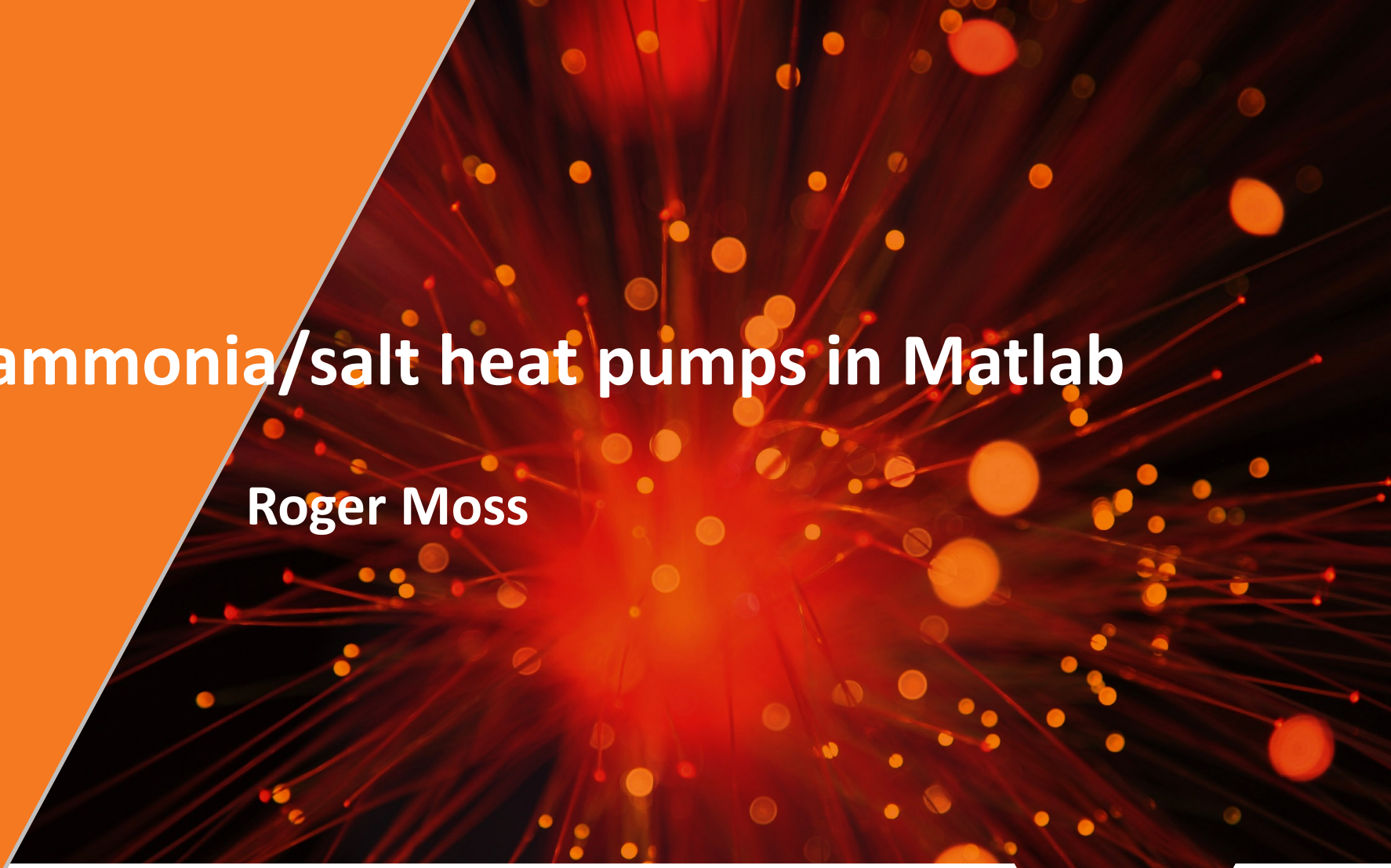
LOT-NET, June 2022

Modelling ammonia/salt heat pumps in Matlab

Roger Moss



STET

MISSION INNOVATION

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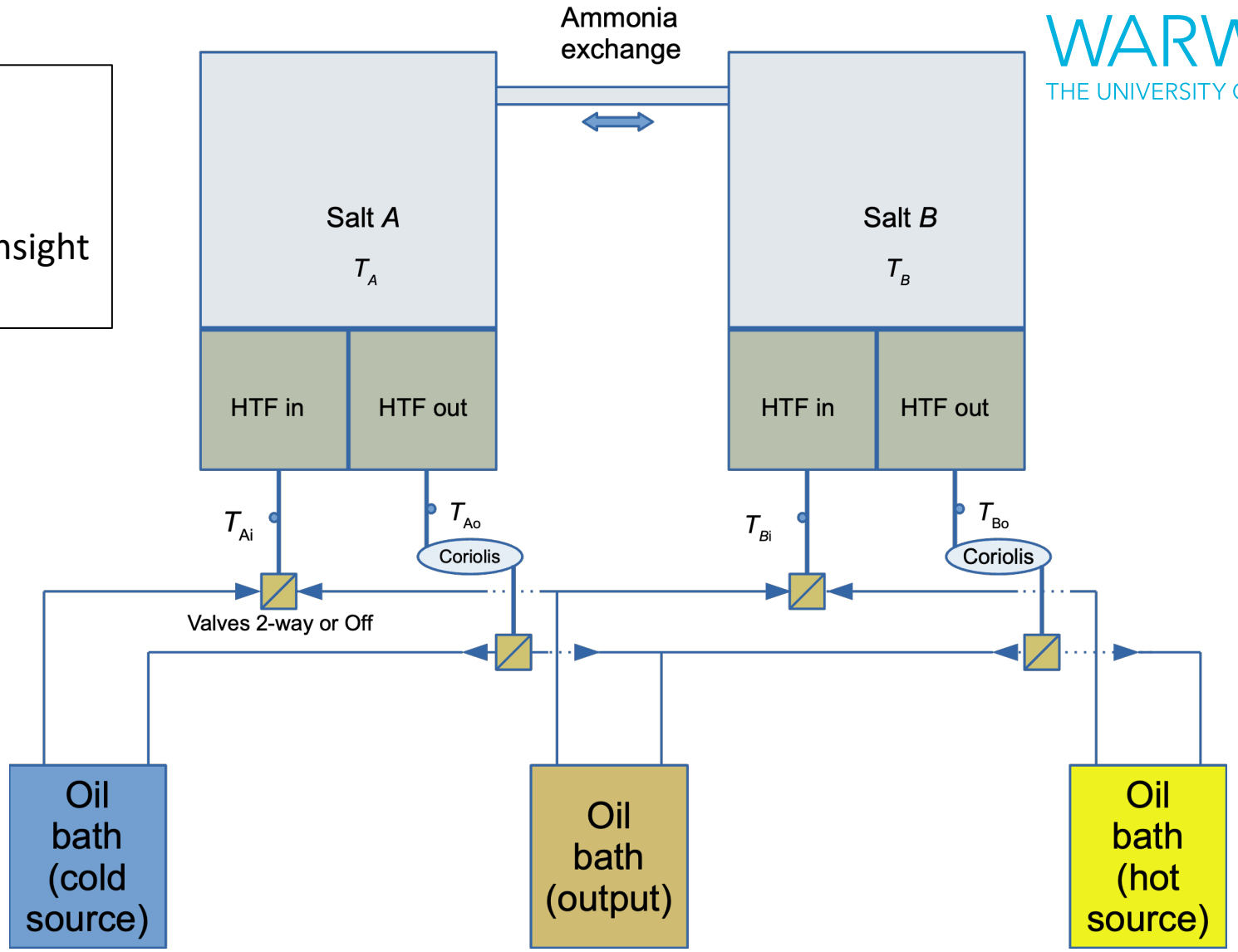
Introduction

Aims:

- Develop a flexible 2D simulation package
- Assess design options and gain insight into key parameters.

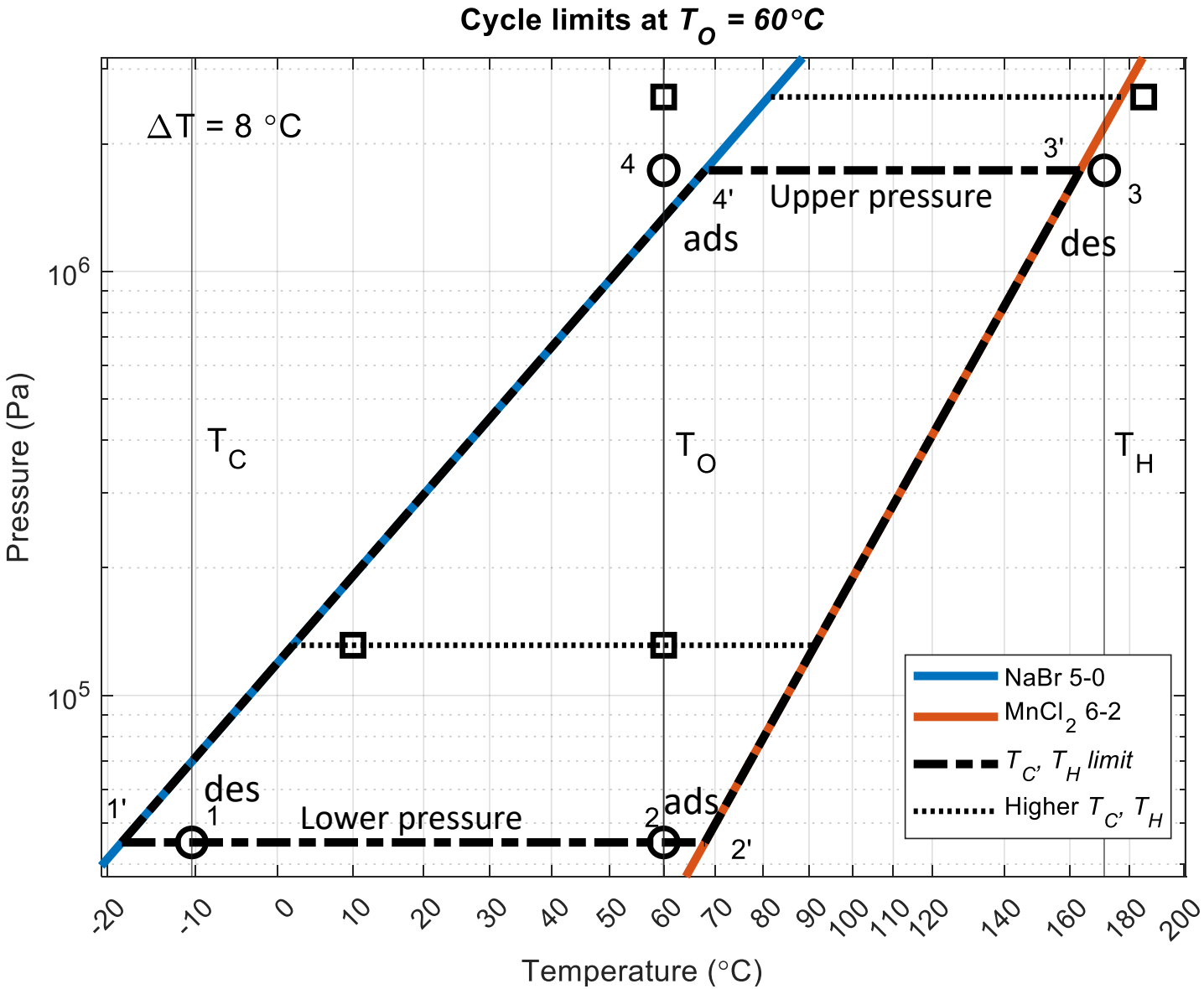
Bench-test heat pump configuration



3 temperatures:

- Cold source T_C
- Delivery (output) T_D, T_O
- Hot source T_H

Supply temperature lower limits for given output temperature & ΔT



- Low temperature salt: **NaBr**
- High temperature salt: **$MnCl_2$**

- Choice of salts is dictated by need to obtain suitable T_C, T_H lower limits
- Must also avoid pressure extremes.

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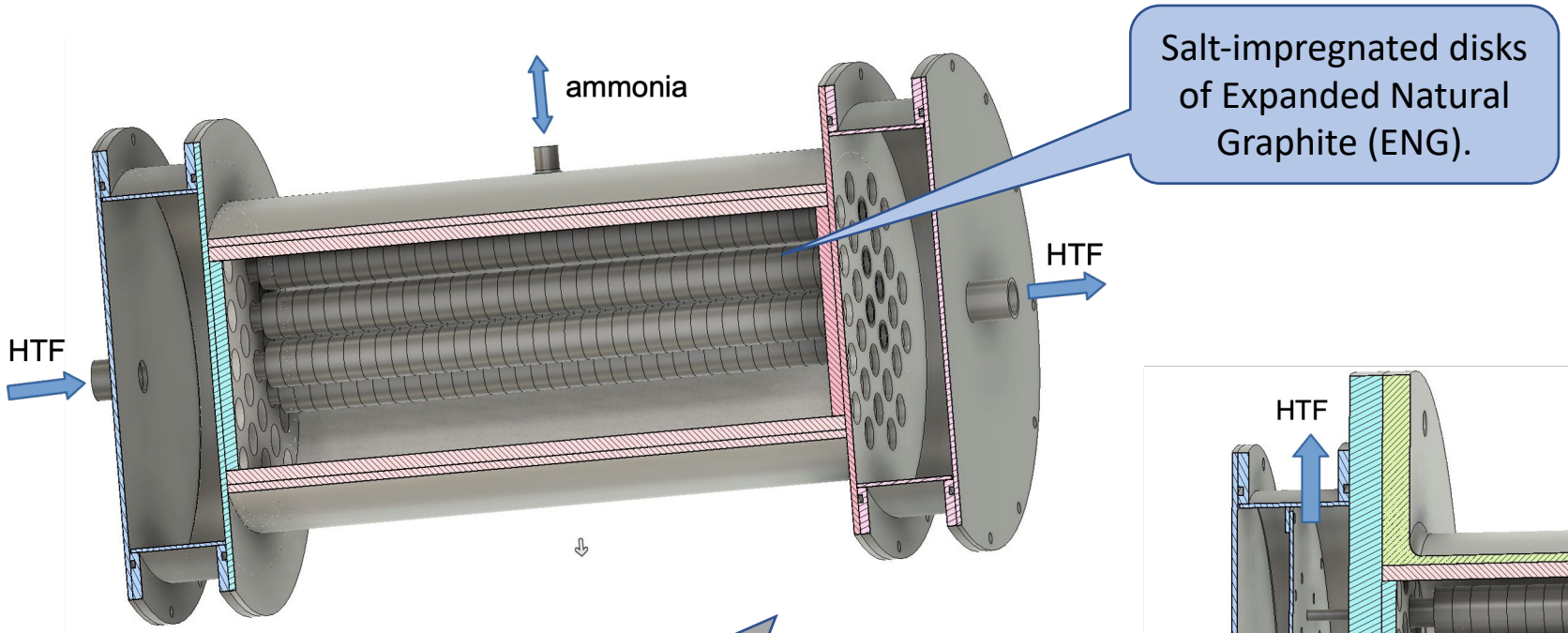
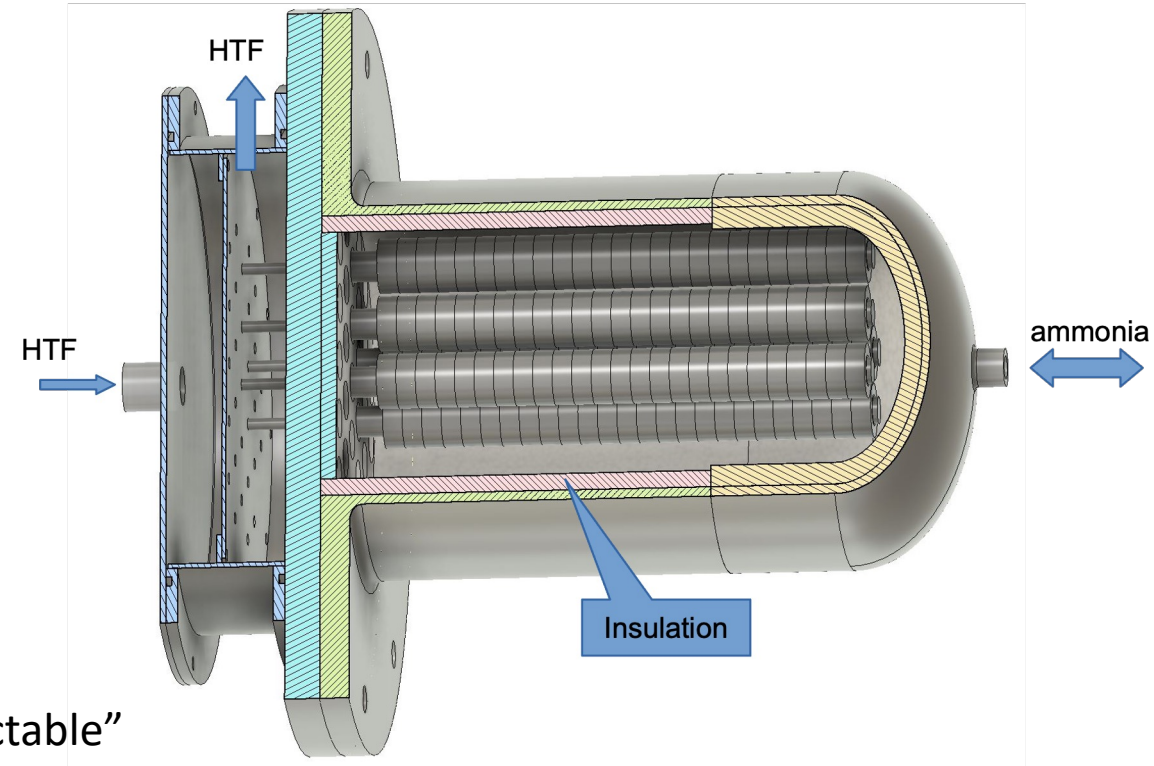
Reactor design philosophies



Salt-impregnated disks of Expanded Natural Graphite (ENG).

"Sealed for life"

Or



"Inspectable"

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Ammonia/salt adsorption code development

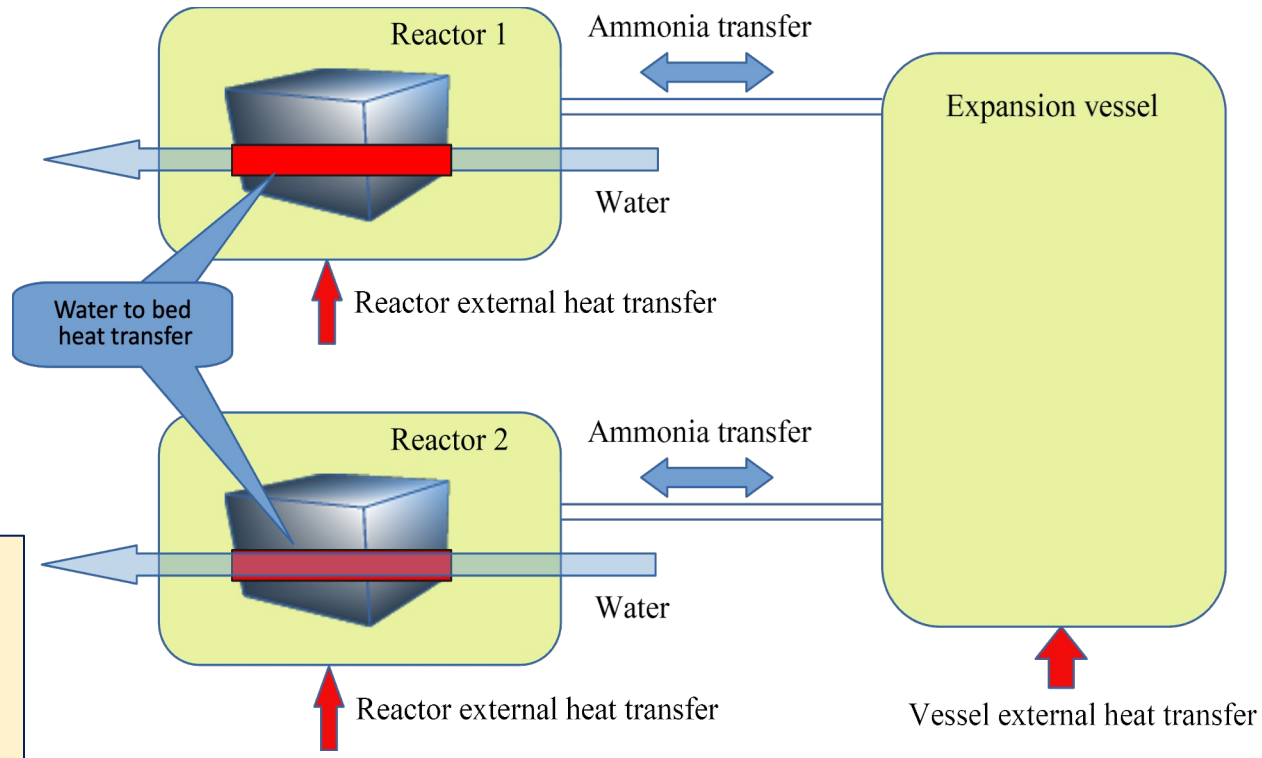
Simulation code:

- 1, 2 or more reactors (+ possible expansion vessel)
- ENG + 1 or more salts per reactor
- Cuboid or cylindrical 2D grid
- Driven by temperature versus time water flows (heat transfer coefficient).
- Models heat transfer and reaction rate

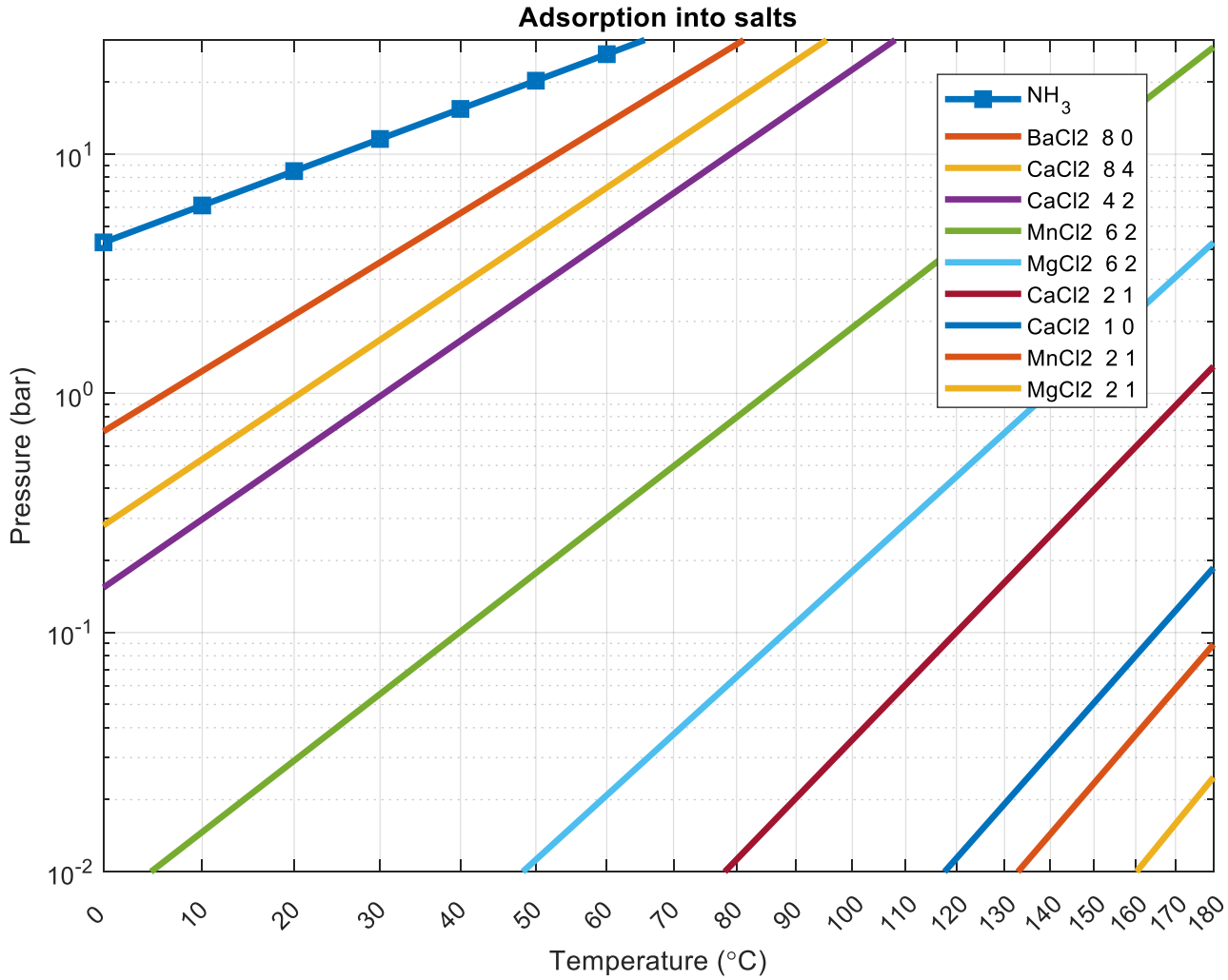
Uses Matlab's ODE15s solver (linked system of ODEs, "Method of Lines").

The code builds a time-derivatives vector for:

- Pressure vessel temperatures
- Temperature of each cell
- Salt ammoniation state in each ENG cell



Equilibrium vapour pressure lines for different salts



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Reaction rate equations

State J to state K (desorption) or K to J (absorption).
Salt mole fraction in each ammoniated state f_J, f_K such that $\sum_{i=1:N} f_i = 1$

Desorption rate equation:

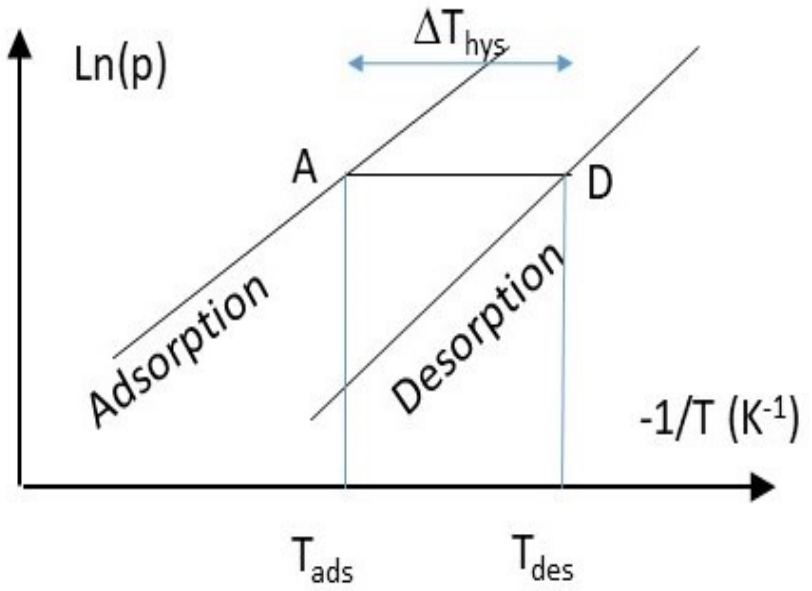
$$\frac{df_K}{dt} = -\frac{df_J}{dt} = A_d \left(f_J + f_K\right)\left(\frac{f_J}{f_J + f_K}\right)^{y_d}\left(\frac{p_{eq,d} - p}{p}\right)$$

$p < p_{EQ}$ causes desorption i.e. positive $\frac{df_K}{dt}$

Adsorption similarly using A_a, y_a, $p_{eq,a}$

$p > p_{EQ}$ causes adsorption i.e. negative $\frac{df_K}{dt}$

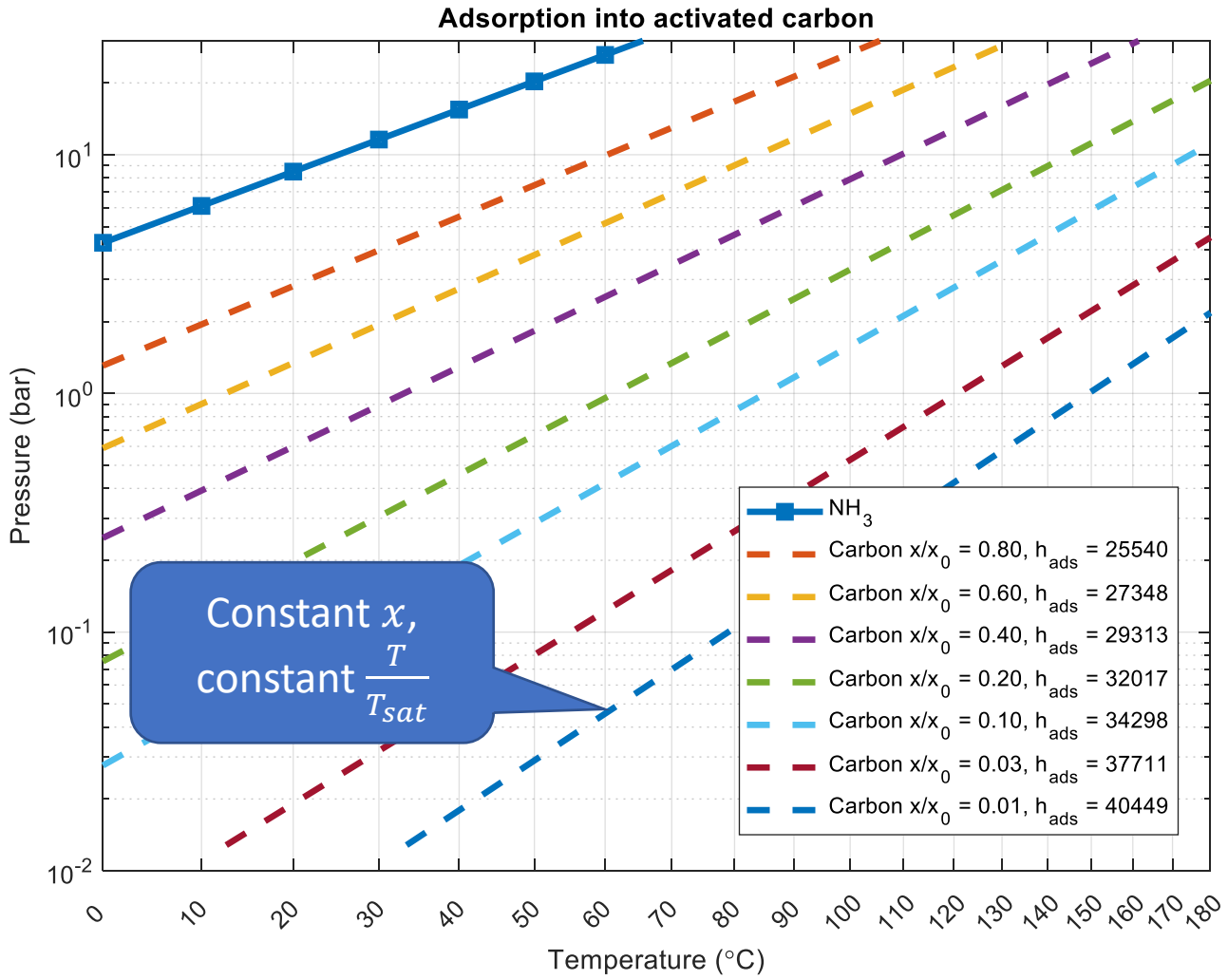
$p_{eq} = e^{\frac{\Delta S}{R} - \frac{\Delta H}{RT}}$ using different $\Delta S, \Delta H$ for each line.



- Pressure assumed uniform (no porosity pressure drop yet)
- Temperature from conduction and heat generation calculation
- No reaction between the adsorption and desorption lines.
- Calculation repeats over all reactions (e.g. 8-4, 4-2, 2-1).
- If using a salt mixture, repeats for each salt.

The rate equation allows Euler integration of the ammoniation state simultaneously with the cell temperatures (ODE15S)

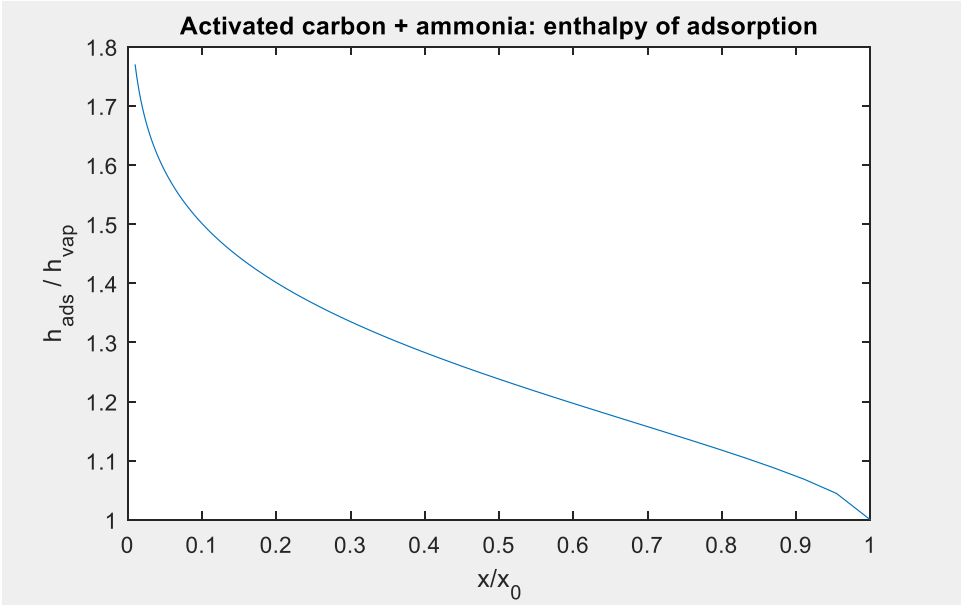
Isostere adsorption lines for activated carbon



Dubinin-Astakhov equation:

$$\frac{x}{x_0} = e^{-k\left(\frac{T}{T_{sat}}-1\right)^n}$$

x_0 = 0.3 kg/kg, k = 7.014,
n = 1.612 (typical).



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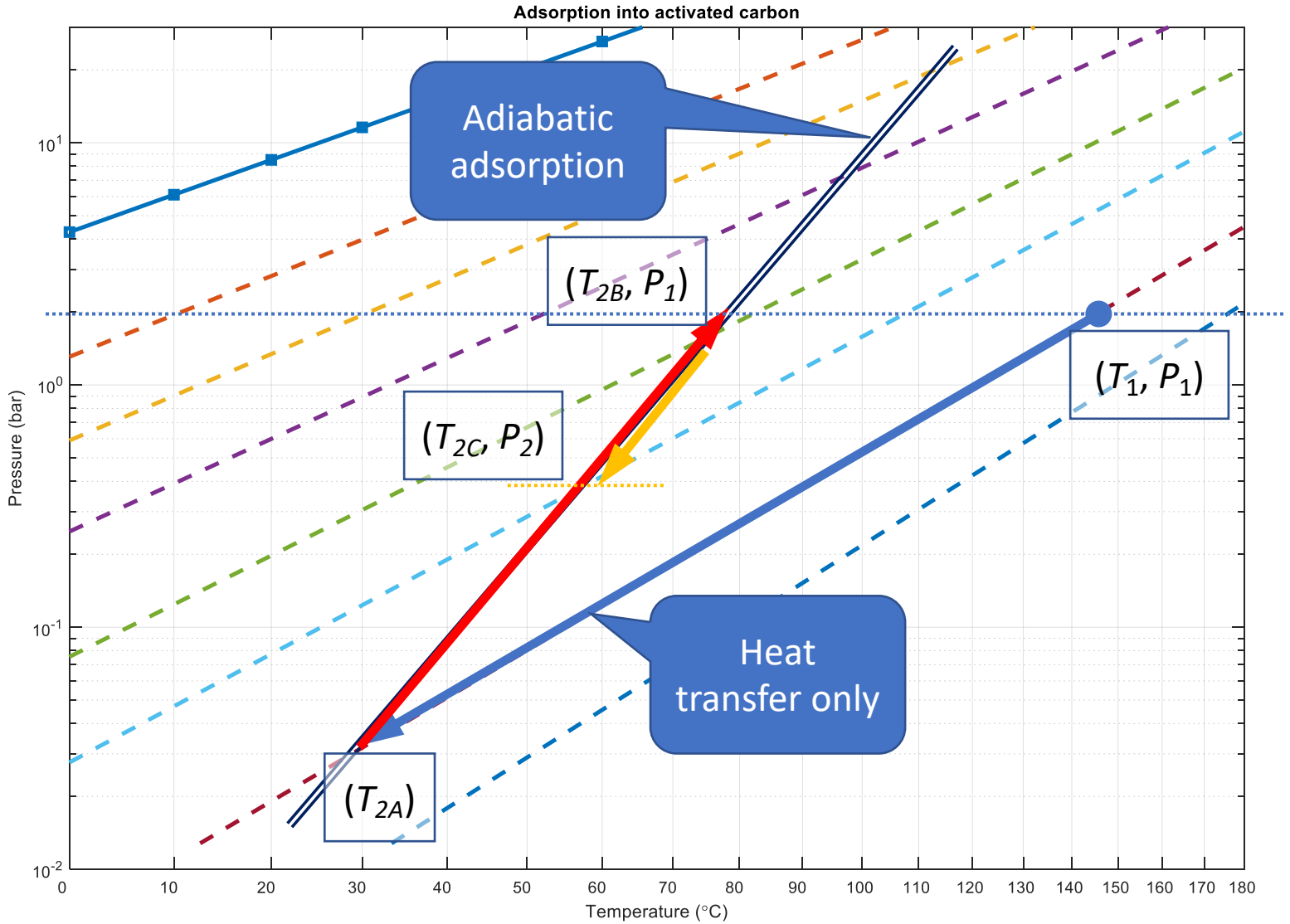
Activated carbon calculation stages (exaggerated scale) for one time step



1 – 2A: 2D heat conduction rate solution from ODE15S, ignoring adsorption

2A – 2B: adsorption temperature change, ignoring conduction

2B - 2C: new system pressure based on reduced gas mass.

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The ODE23 state variables (`U`, `u0`, `uR`)

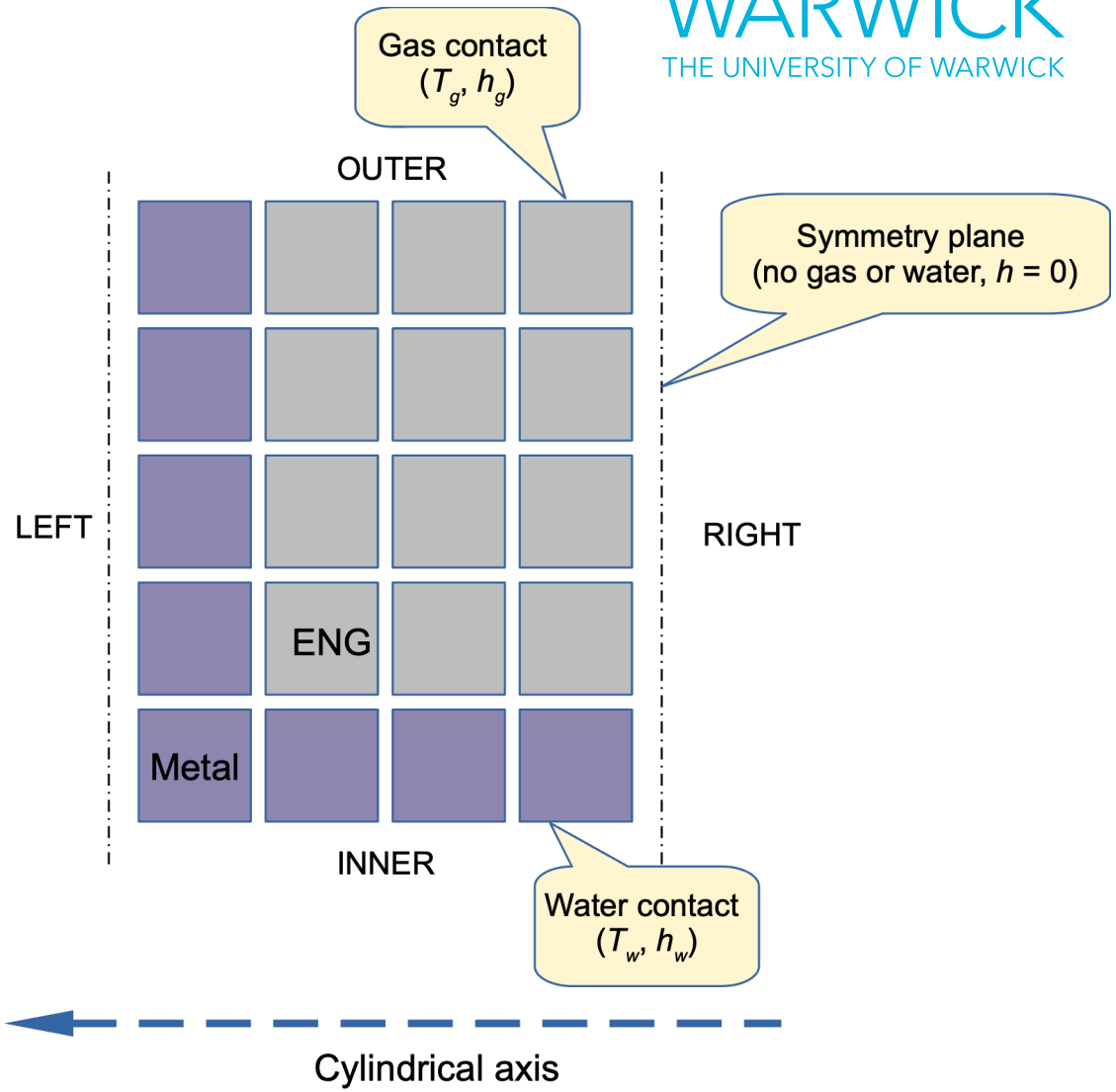
The Matlab ODE solver is invoked as follows:

```
[t, Uout] = ode15s(@rs_tderiv, tspan, U, options);
```

- `ode15s` picks suitable time steps and iterates without requiring any user-generated iteration code.
- `@rs_tderiv` is a handle to the function that converts the state vector `U` into its time derivative. U contains both cell temperatures and salt ammoniation states; for ease of programming, the code splits it into a pair of structured variables u0, uR, calculates the derivatives and reassembles them into a vector DU.
- `tspan` defines the time period to be simulated
- `U` is just a set of initial values for the state vector.

Typical grid definition

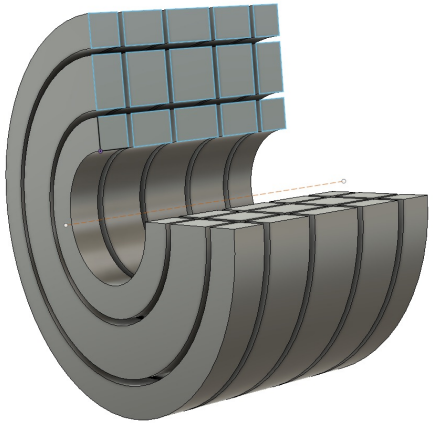
```
iR = 1;
rig.Reactor(iR).gVol = 0.5E-3;  % reactor void space
rig.Reactor(iR).IOLR.gas = logical([0 1 0 0]);
rig.Reactor(iR).IOLR.metal = logical([1 0 1 0]);
rig.Reactor(iR).IOLR.water = logical([1 0 0 0]);
rig.Reactor(iR).m = 0;  % linear
rig.Reactor(iR).zlen = 0.3;  % width for m=0 cases
rig.Reactor(iR).mcs = 20e3;  % shell m*c
rig.Reactor(iR).mdotc_fluid = 20;
rig.Reactor(iR).repeats = 10;
rig.Reactor(iR).dim(1).gridx = linspace(0.01, 0.02, 8)';
rig.Reactor(iR).dim(2).gridx = linspace(0, 0.04, 6);
rig.Reactor(iR).gap = 0.2E-3; % metal-ENG gap
rig.Reactor(iR).h_fluid = 20;  % W/m2K
rig.Reactor(iR).h_gas = 5;  % W/m2K

rig.Reactor(iR).Salt = salt_reaction_props('BaCl2');
rig.Reactor(iR).Salt(1).saltFrac = 0.4;
```



Grid cells are either ENG+salt or metal (plate, tube or fin), with contact resistance between metal and ENG.

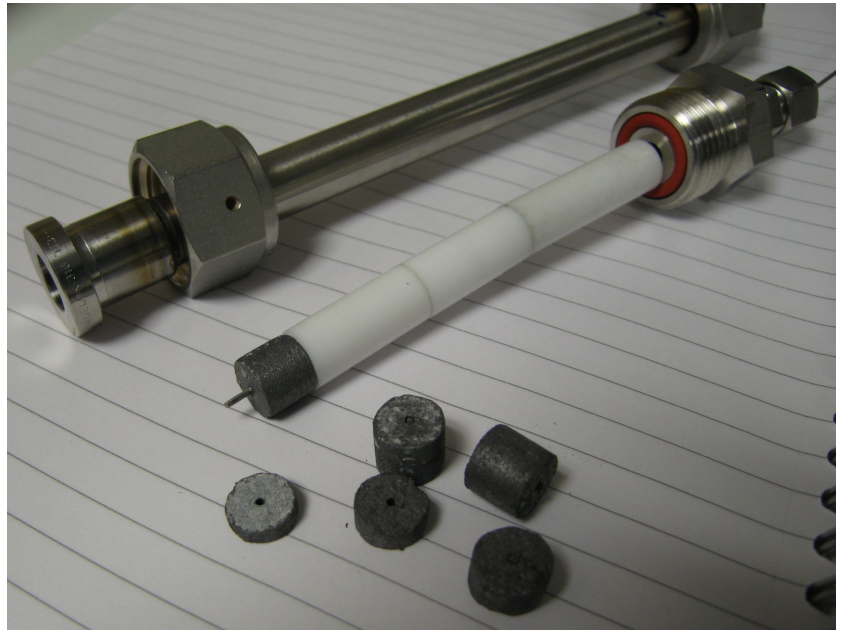
Ability to model ENG rings or pellets:

- 1D or 2D structured grids
- Cuboid (*x*,*y*) or cylindrical (*r*,*z*)



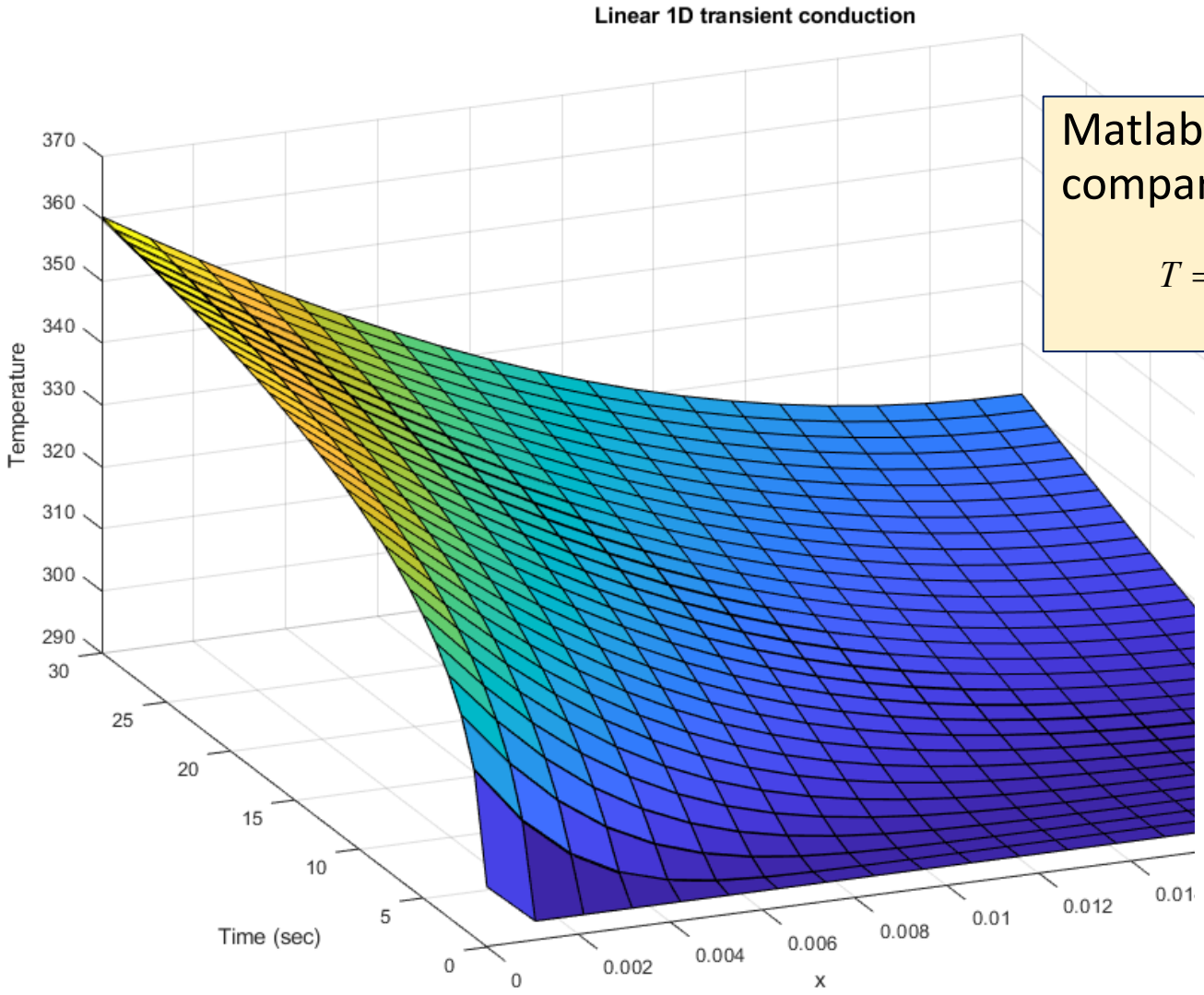
No heat flux in the third direction.

Salt/ENG “kebab”
(Hinmers, Energies, 2022)



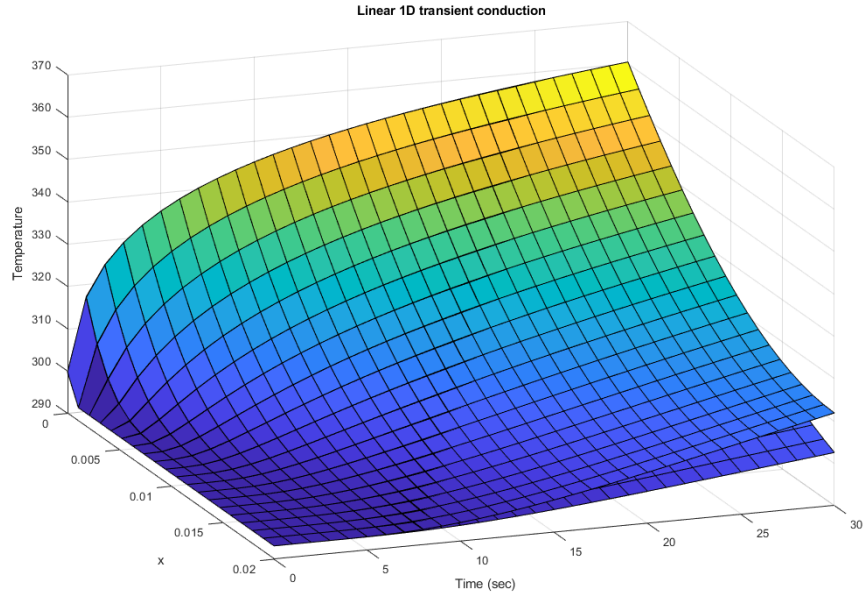
Cycling rig salt/ENG pellets

Conduction equation validation



Matlab solution with a step in water temperature compared with the semi-infinite analytical solution

$$T = T_2 + (T_1 - T_2)\left[\operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha t}}\right) - e^{\left(\frac{hx}{k} + \frac{\alpha h^2 t}{k^2}\right)} \operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha t}} + \frac{h\sqrt{\alpha t}}{k}\right)\right]$$



ump

Ammonia transport through ENG *(in progress)*

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Matrix solution of a resistance network

Assume Darcey's law $Q = \frac{Ak}{\mu}\frac{dP}{dx}$ for cell-to-cell transport.

Permeability $k \approx 2\times10^{-12}$ m² (n.b. different in-plane and perpendicular)

Volume flow rate $Q_1 = \frac{T_1 p_1}{\mu}$ etc

$q_1 = Q_1 - Q_2 + Q_{13} - Q_{14}$ etc

(assume constant density & viscosity).

Column vectors $\boldsymbol{p}, \boldsymbol{q}, \boldsymbol{Q}$:

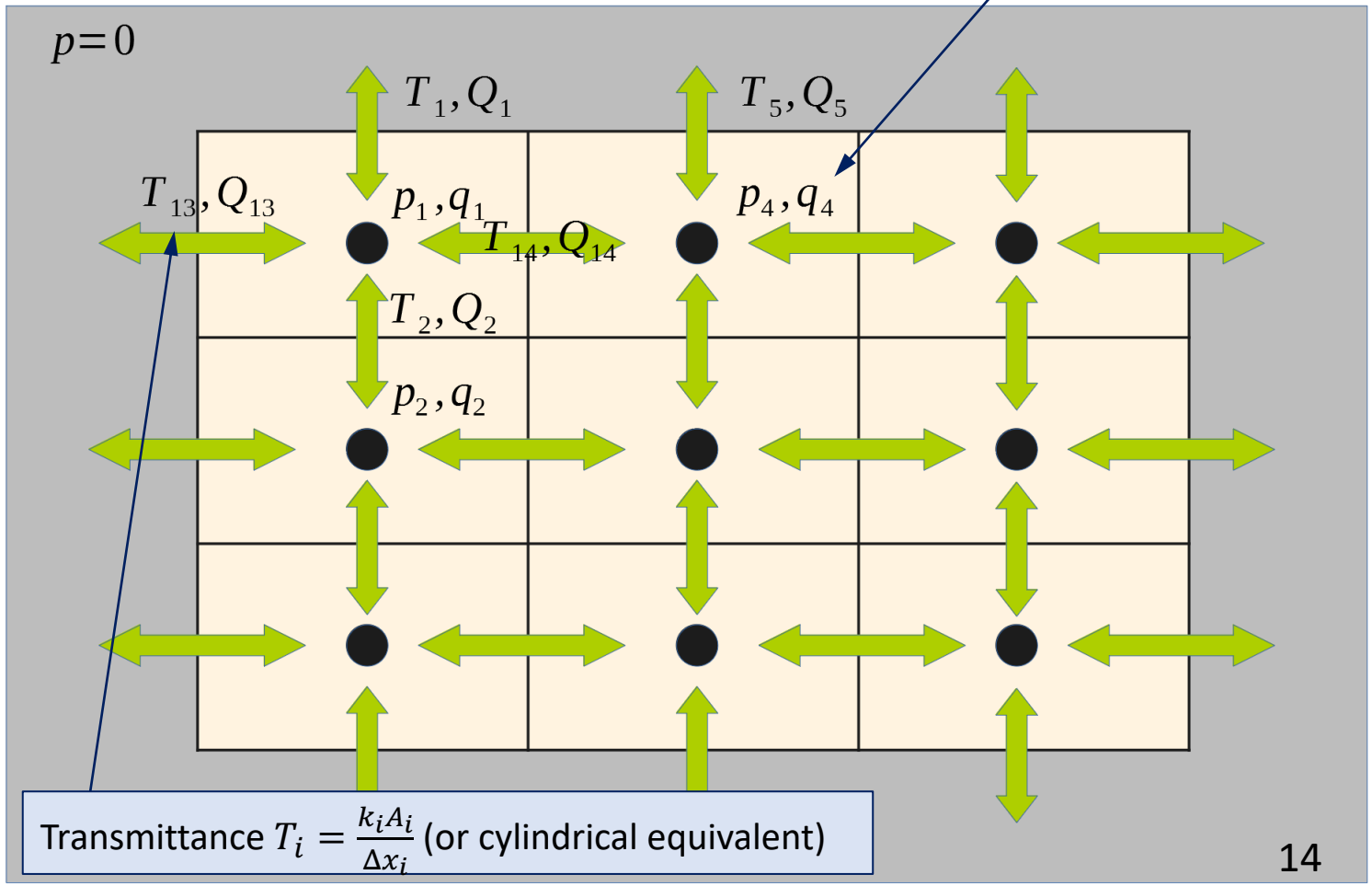
$$\boldsymbol{JQ} = \boldsymbol{q},\ \boldsymbol{Q} = \frac{k}{\mu}\boldsymbol{T}\boldsymbol{p}.$$

Solve:

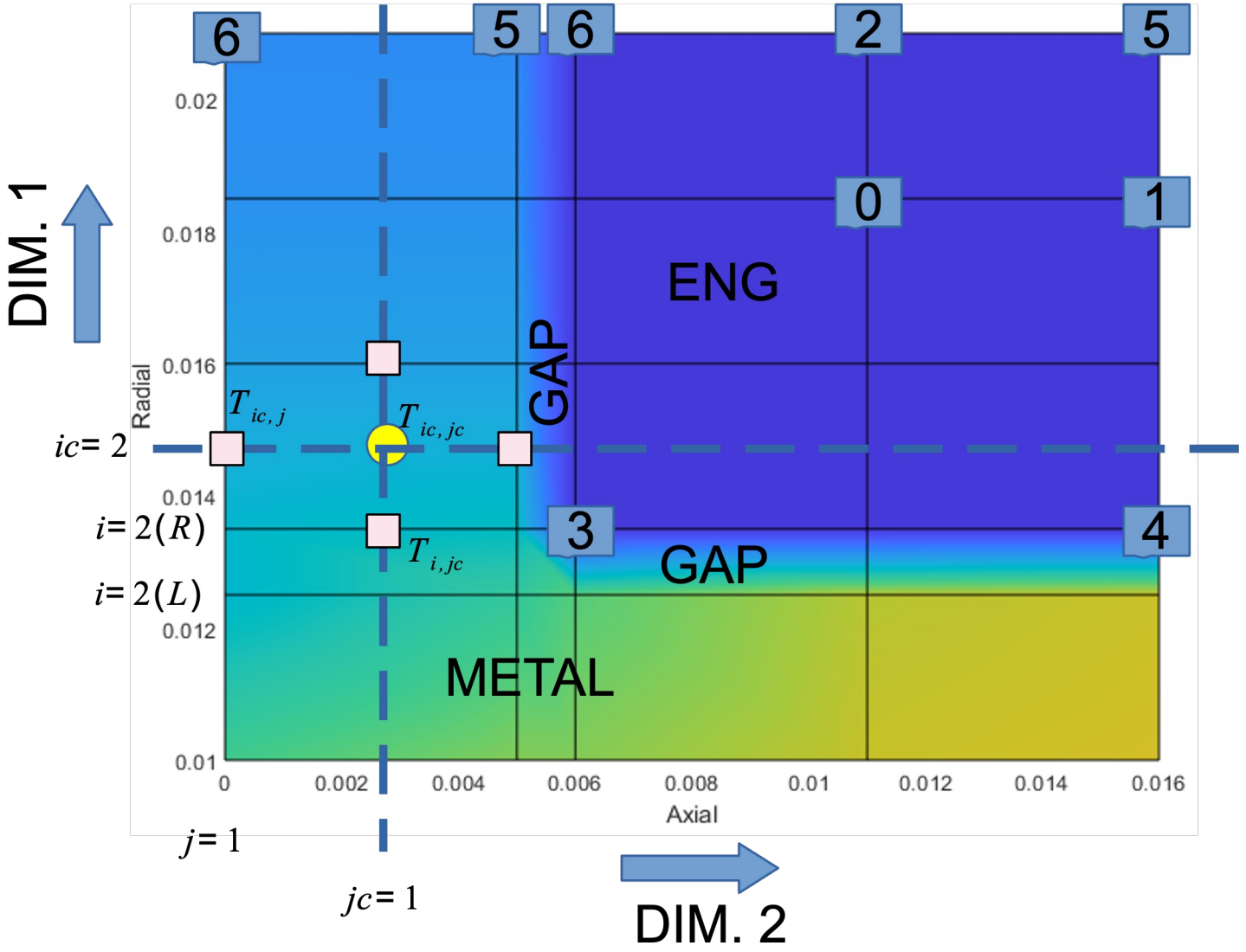
$$\boldsymbol{p} = \frac{\mu}{k}(\boldsymbol{JT})^{-1}\boldsymbol{q}$$

$$\boldsymbol{Q} = \boldsymbol{T}(\boldsymbol{JT})^{-1}\boldsymbol{q}$$

Cell adsorption & desorption rates q from the reaction rate equation.



Plotting



- The solver calculates temperatures at cell centres.
- Matlab surface plotting uses cell corner values.
- The code interpolates values from centres to corners.

Heat transfer to reactor shell and expansion vessel.

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➢ Absorption, desorption and temperature changes lead to gas flow between vessels.

At each time step:

i. Use mass of non-absorbed ammonia to calculate the system pressure.

ii. Calculate the rate of pressure change: $$\frac{\dot{P}}{P}\sum_{0:N}\left(\frac{\gamma-1}{\gamma}c_v m_i T_{R,i}\right)=P\sum\left(\dot{m}_i v_{io,i}\right)$$

iii. Calculate adiabatic mass flow rate between vessels $$\dot{m}_{RE,i}=\dot{m}_{D,i}\left(\frac{T_{io}}{T_R}\right)-\frac{V_{R,i}}{\gamma R T_R}\dot{P}$$

iv. Unsteady energy equation for each vessel - find rate of change of mixed-out temperature.

$$\frac{\mathrm{d}U}{\mathrm{d}t}=\dot{Q}_{in}+\dot{W}_{in}+\sum\dot{m}_{in,j}h_j \qquad \therefore \quad \left(m_w c_w+m_g c_v\right)\frac{\mathrm{d}T_{R,i}}{\mathrm{d}t}=P\left(\dot{m}_{D,i}v_{Dio}-\dot{m}_{RE,i}v_{Eio}\right)+\dot{Q}_{in}$$

$$\left(m_w c_w+m_g c_v\right)\frac{\mathrm{d}T_E}{\mathrm{d}t}=P\sum_{1:N}\left(\dot{m}_{RE,i}v_{Eio}\right)$$

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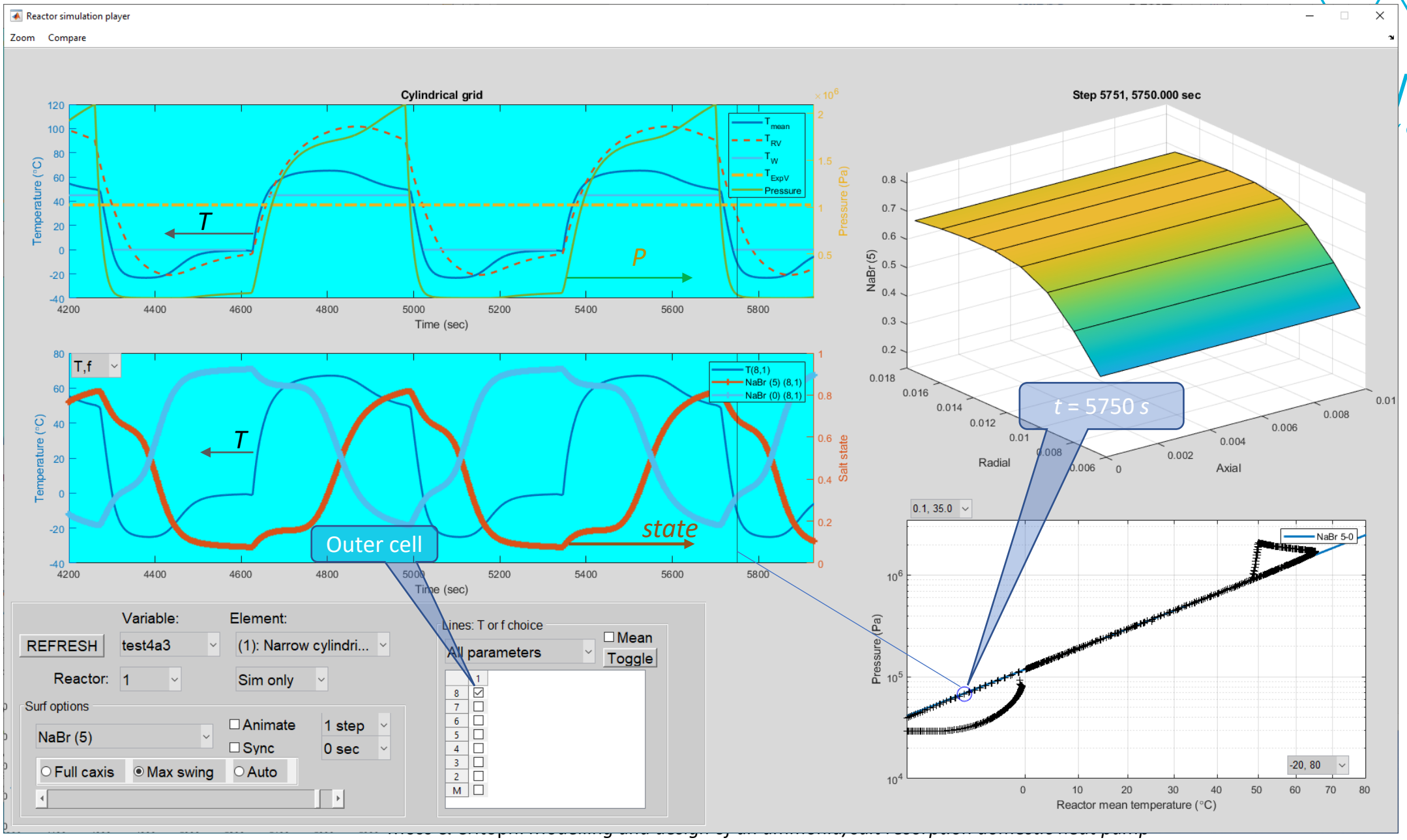
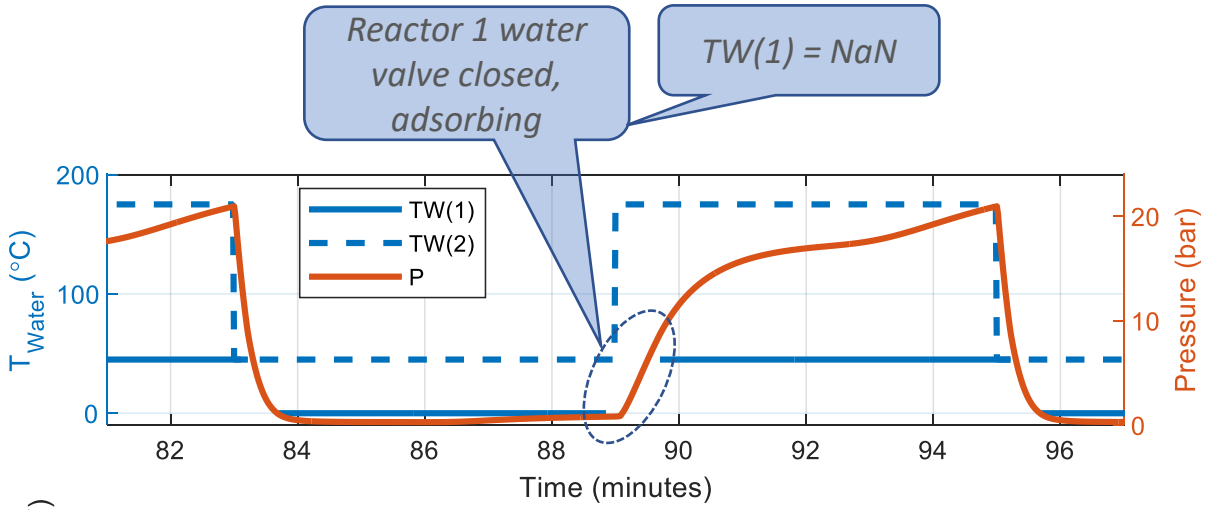
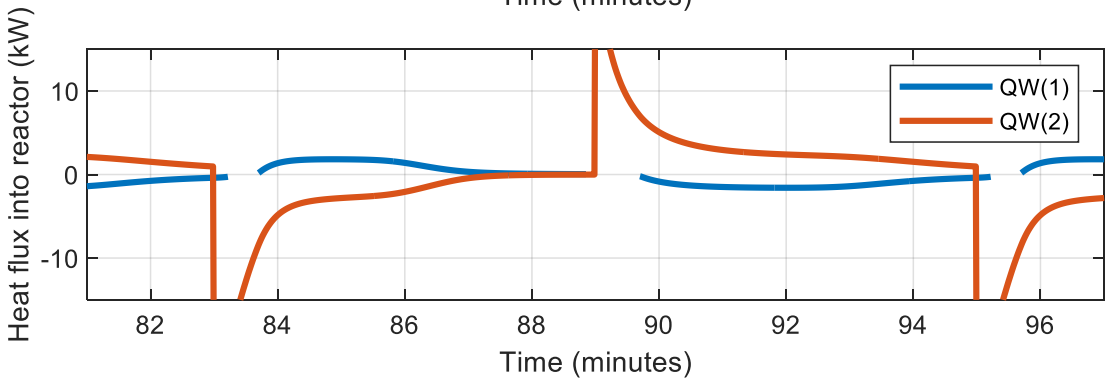
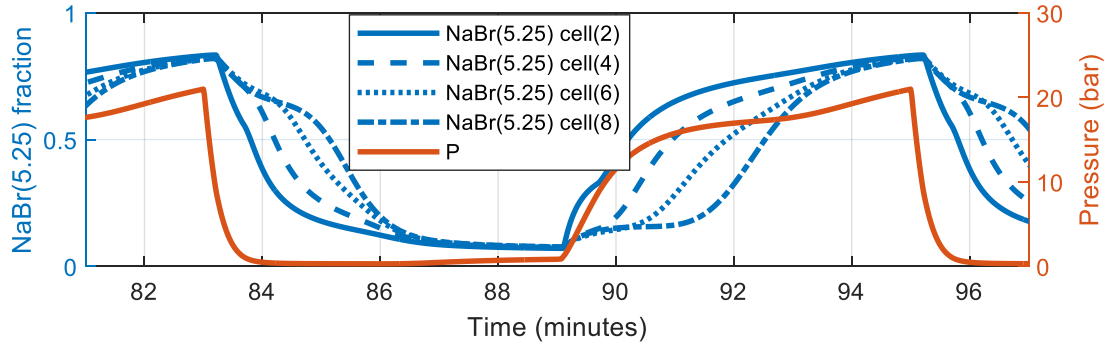
Output viewer displays overall and local parameters for each reactor

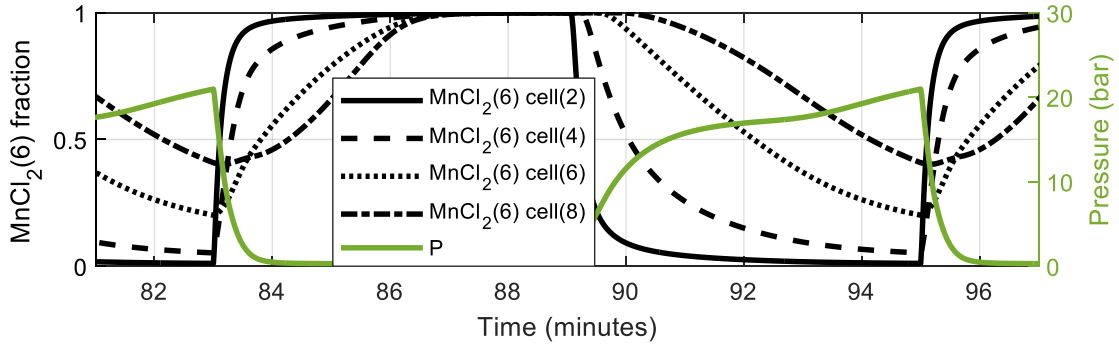


Cycle parameters: temperature, heat flux and ammoniation state.

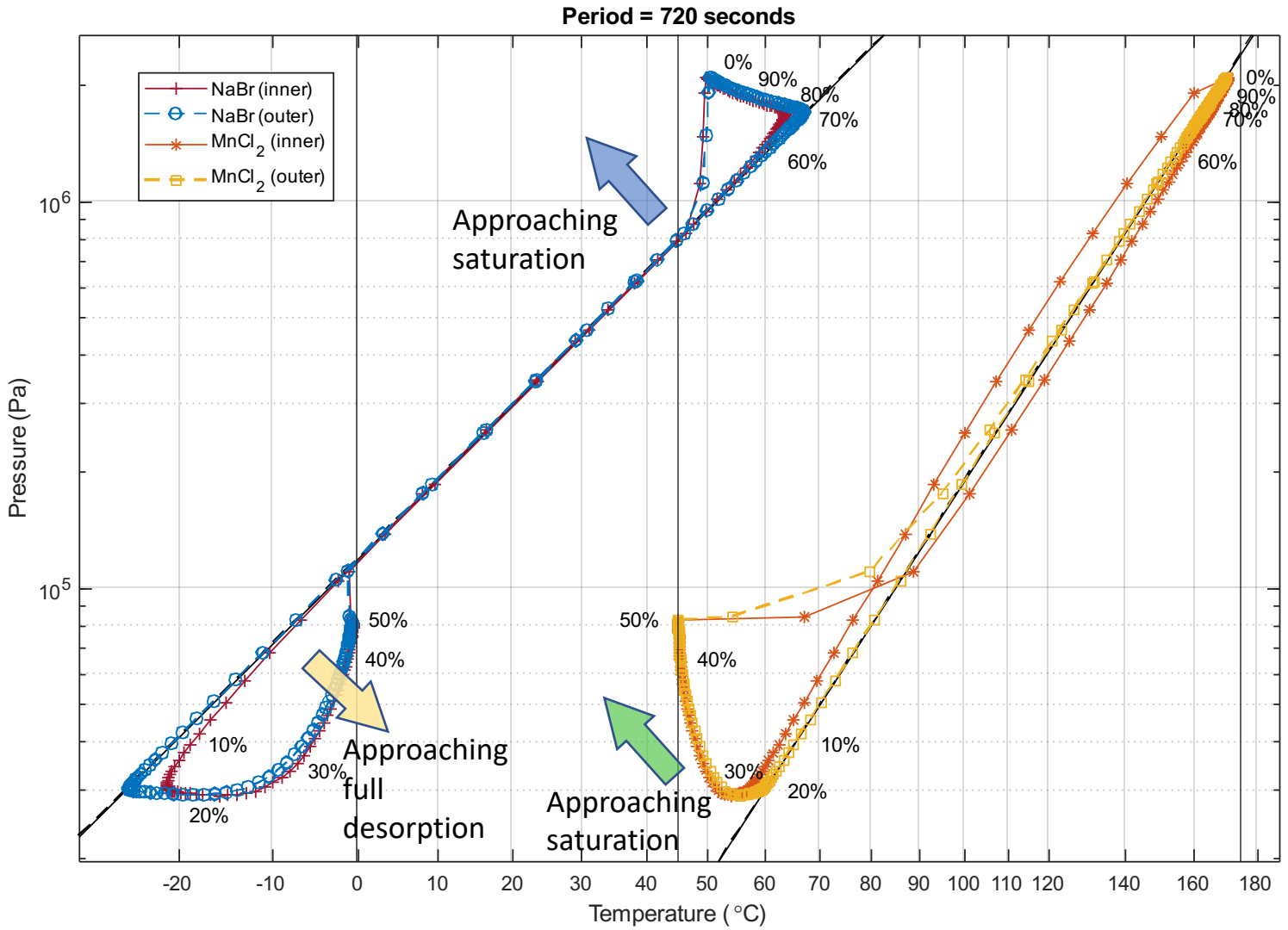




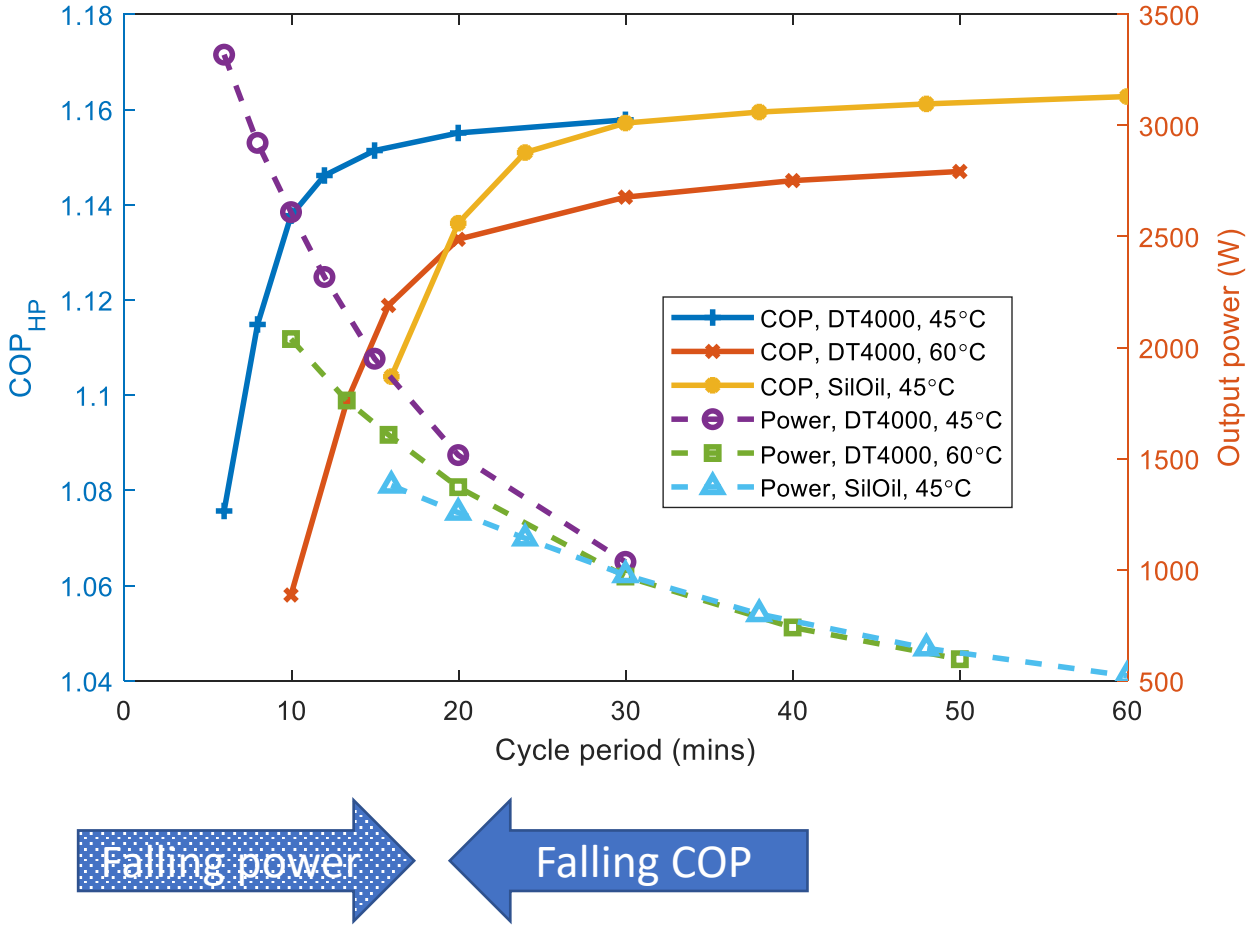




Clapeyron diagram for both reactors.



COP and power density as a function of output temperature T_O.



Comparison of two heat transfer fluids:

- DowTherm 4000 (water-glycol)
- Huber SilOil 235.

Good heat transfer and low sensible heat capacity are essential.

Conclusions

- A 2D unsteady solver for heat transfer and salt/ammonia reaction kinetics has been written in Matlab.
- A NaBr/$MnCl_2$ heat pump has been simulated.
- Optimum cycle period is a compromise between COP and power output. Low sensible heat capacity (shell insulation) and good heat transfer are essential.
- A mass transfer model has been written for ammonia within the ENG (under development).
- The salt reaction model is being extended to include ENG adsorption