Ammonia-Salt Research at Warwick

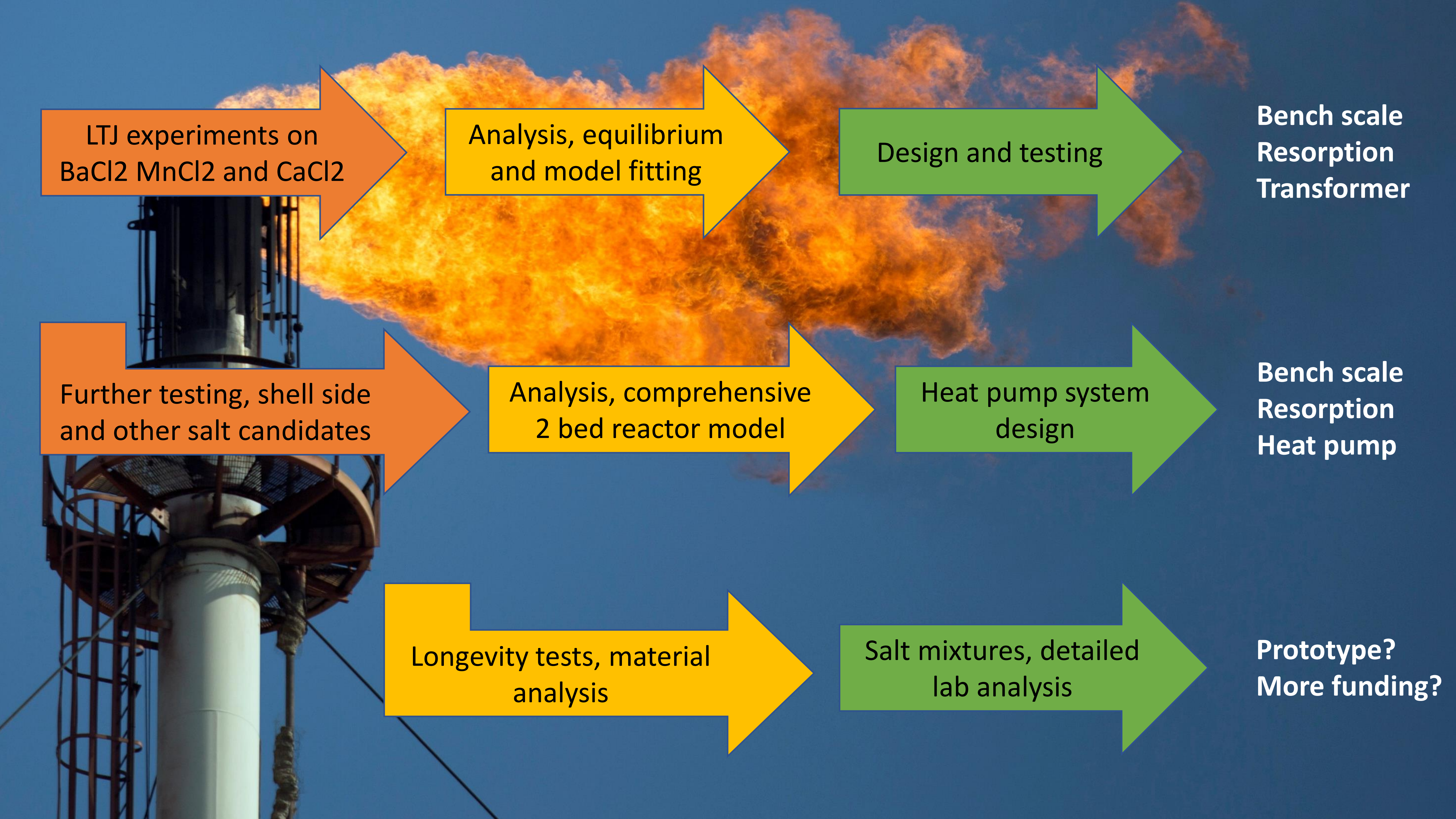
MI meeting

8th October 2020

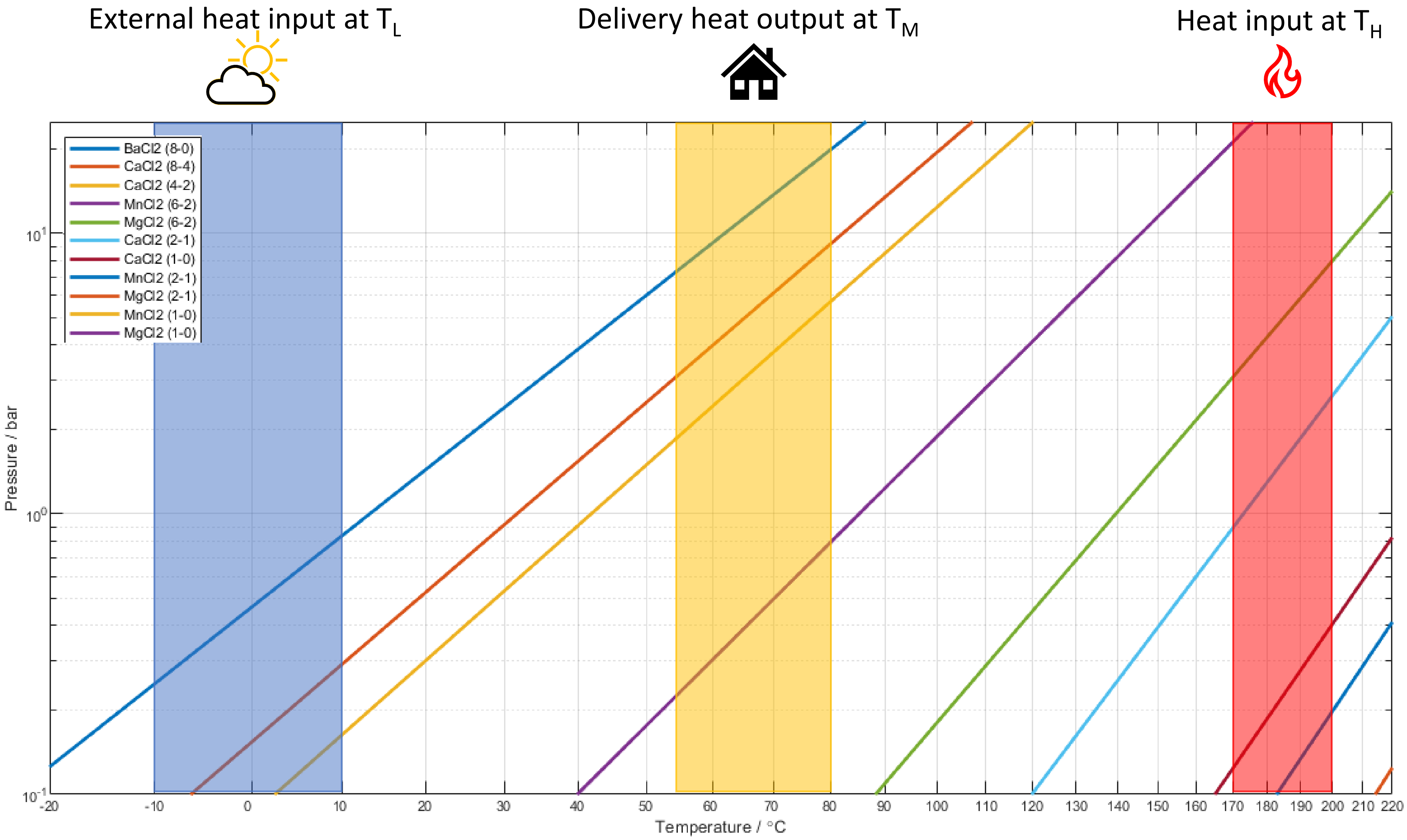
ENERGY RESEARCH ACCELERATOR

EPSRC
Engineering and Physical Sciences Research Council

WARWICK
THE UNIVERSITY OF WARWICK

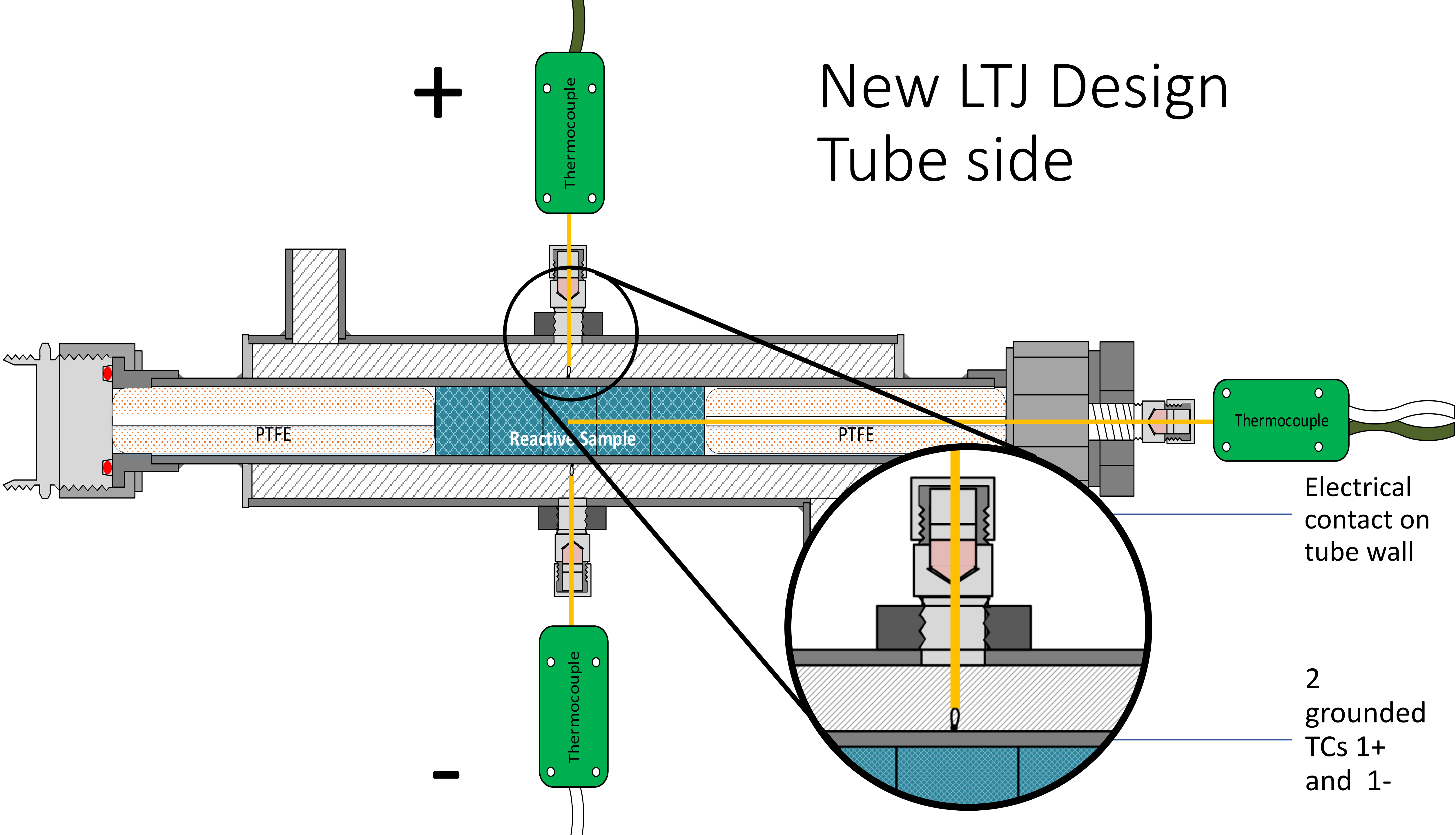


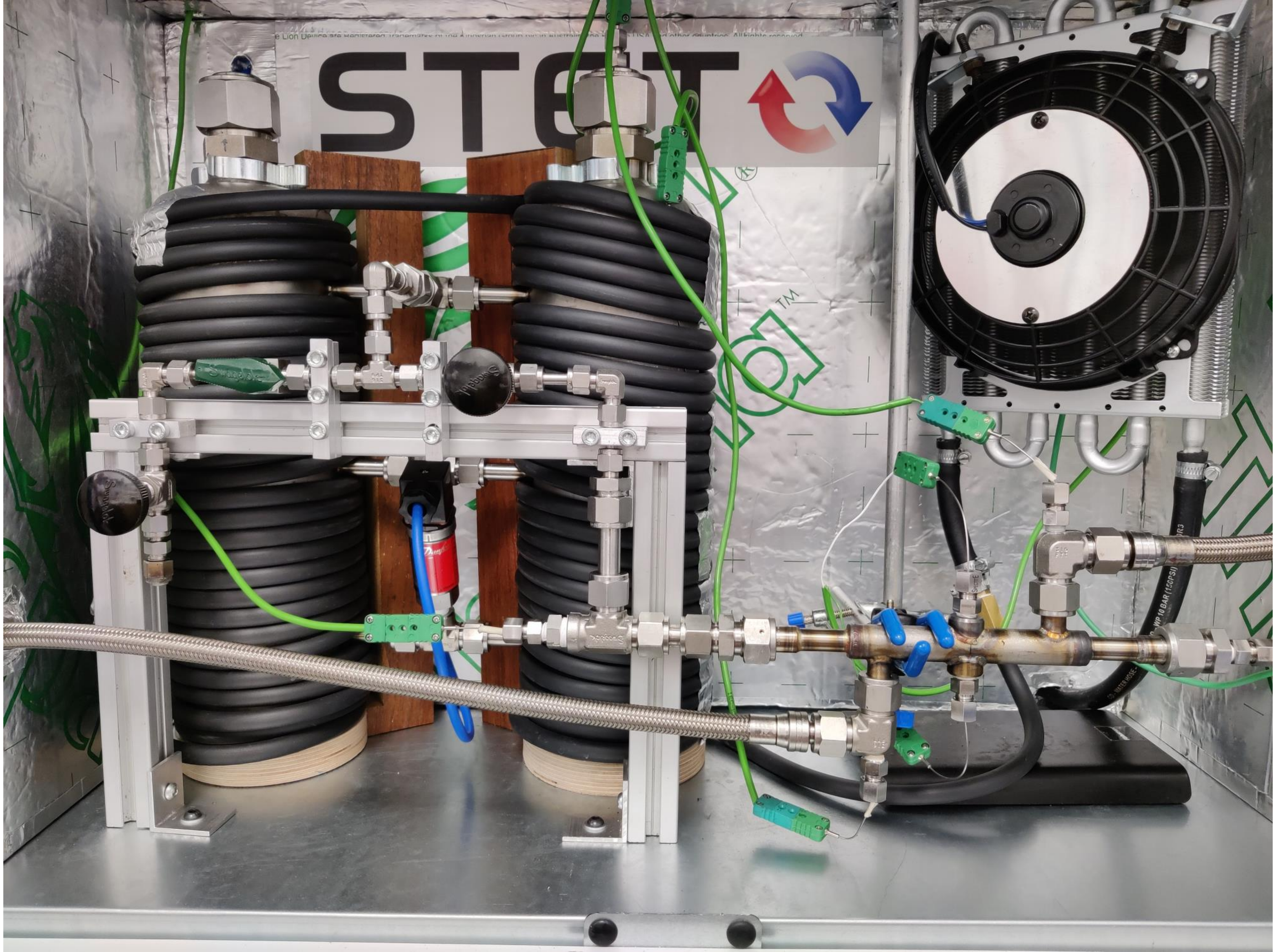
LTJ experiments on BaCl2 MnCl2 and CaCl2
Analysis, equilibrium and model fitting
Design and testing
Bench scale Resorption Transformer
Further testing, shell side and other salt candidates
Analysis, comprehensive 2 bed reactor model
Heat pump system design
Bench scale Resorption Heat pump
Longevity tests, material analysis
Salt mixtures, detailed lab analysis
Prototype? More funding?

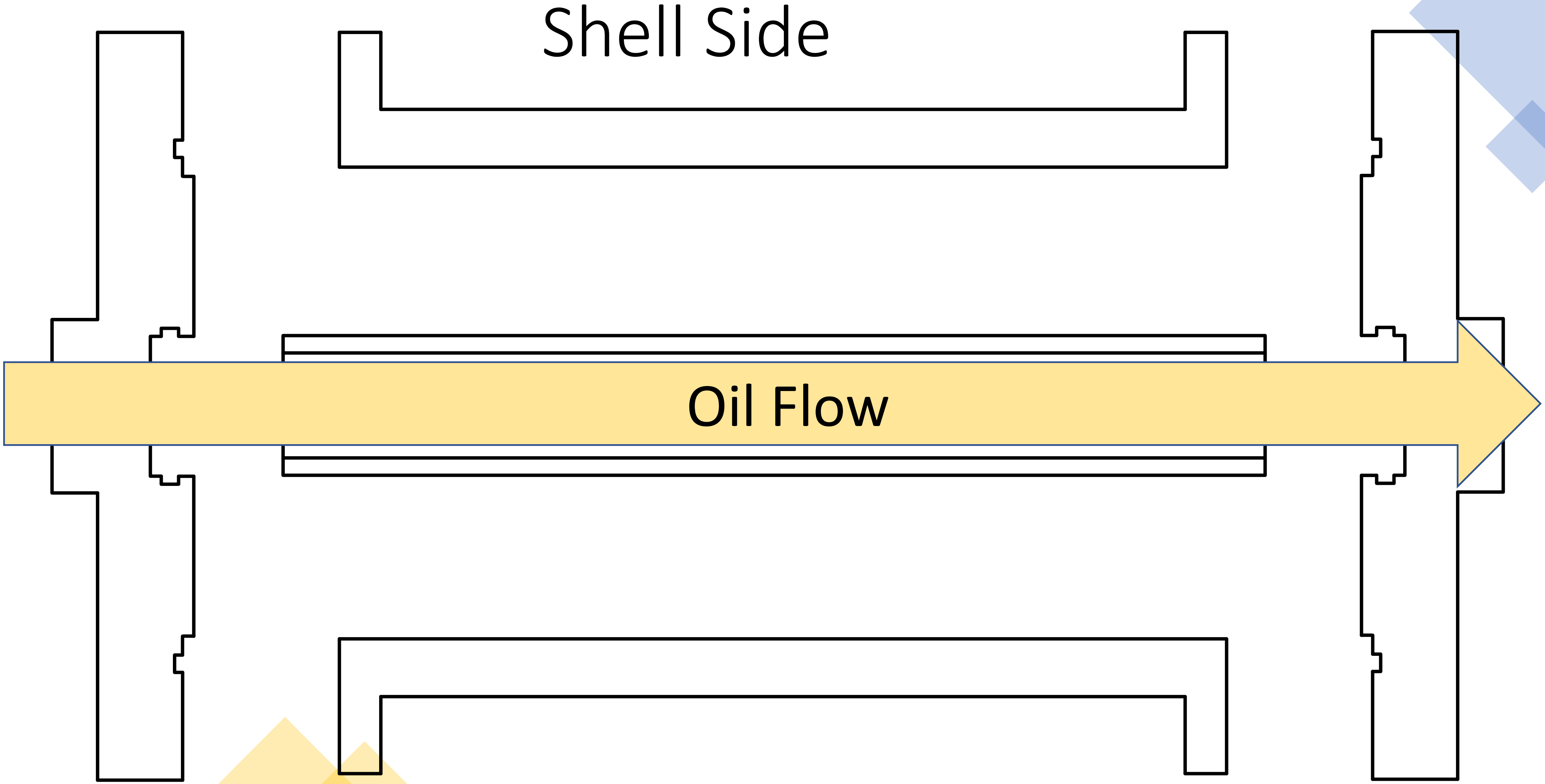


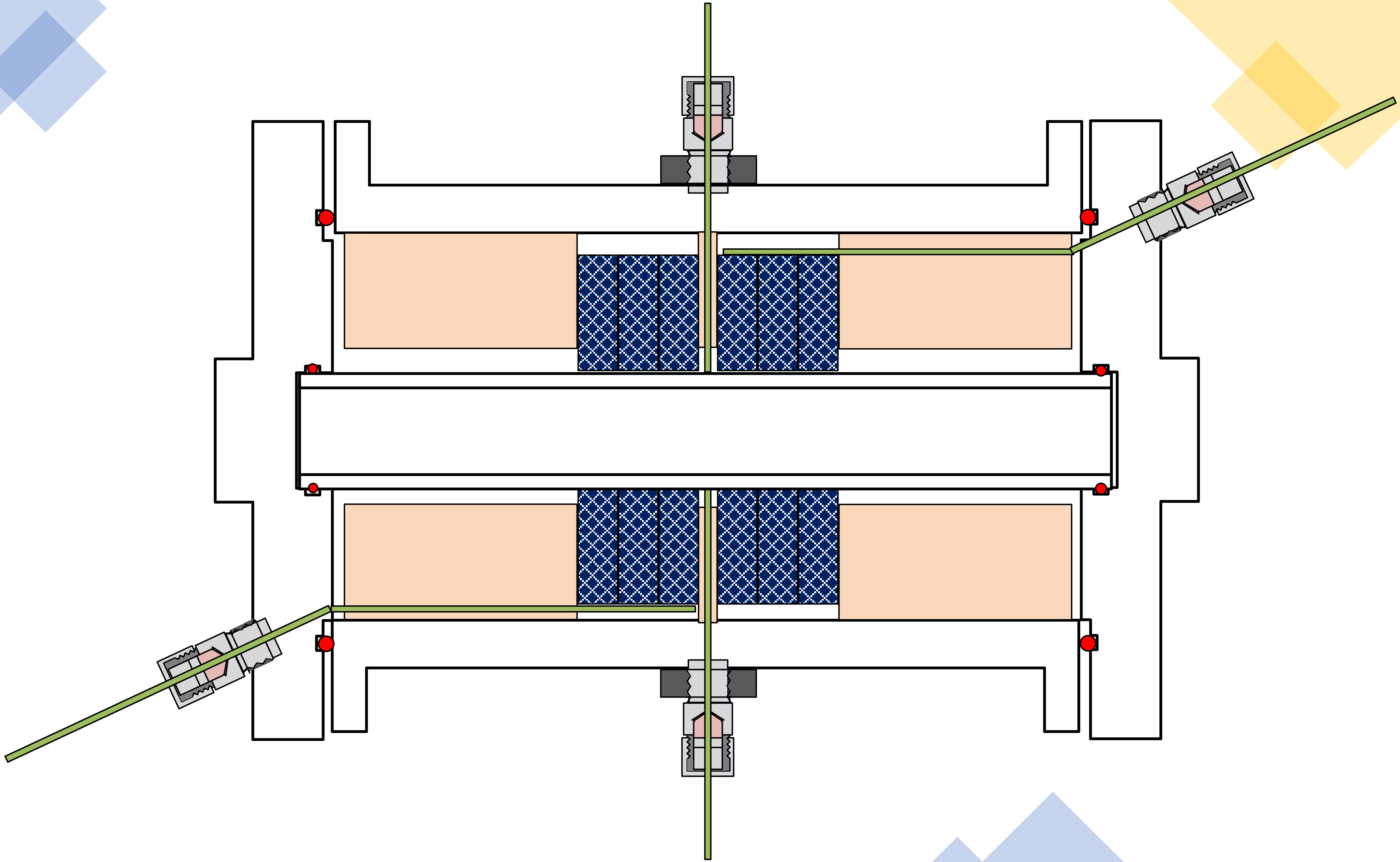
BaCl2 (LTS) with $MnCl_2$ as HTS. LTJ performance of LP $BaCl_2$ currently ongoing.
Other salt pairings to be considered based on results.

New LTJ Design
Tube side




STET

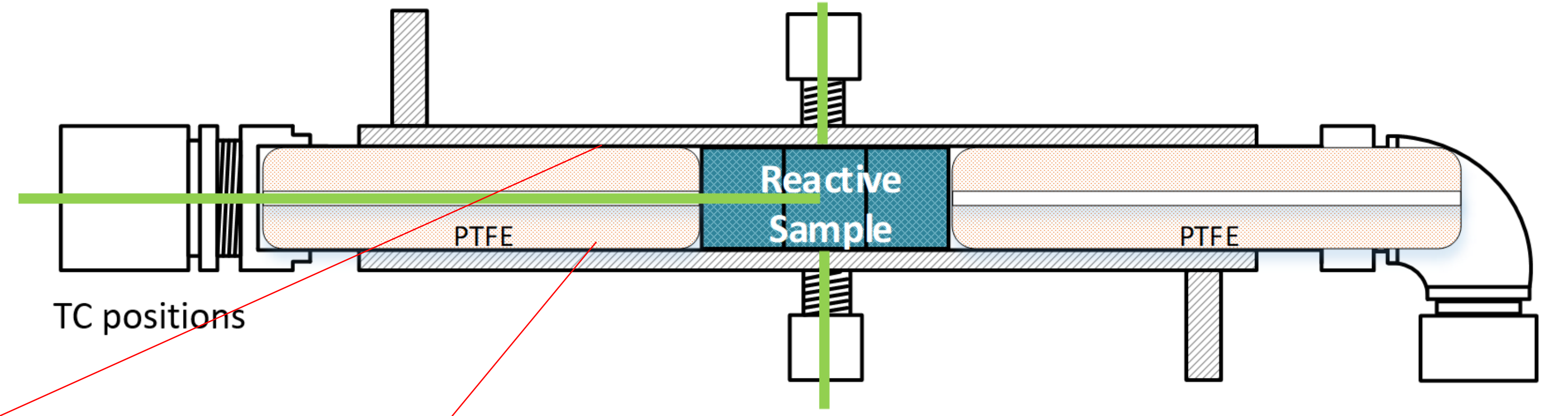

Shell Side
Oil Flow



LTJ Test modelling

Large Temperature Jump Reactor

1-D axi-symmetric model



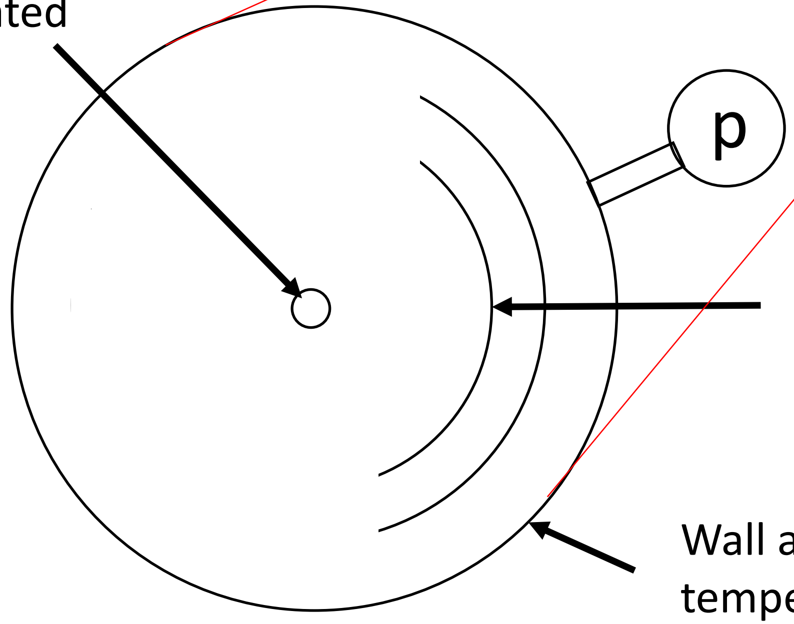
½ inch pipe centre

1 inch pipe jacket

PTFE to fill heated volume

O-ring Swagelok face seal fitting

Centre thermocouple temperature to be simulated



Pressure to be simulated

n elements of ENG and salt at radius *r*

Wall at measured temperature (boundary condition)

Rate equations (2 reactions):

$m_{ads\ 1}$	$m_{ads\ 2}$	$m_{ads\ 3}$
$m_{salt\ 1}$	$m_{salt\ 2}$	$m_{salt\ 3}$

$m_{ads\ 1}+dm_{ads\ 1}$	$m_{ads\ 2}+dm_{ads\ 2}$	$m_{ads\ 3}+dm_{ads\ 3}$
$m_{salt\ 1}+dm_{salt\ 1}$	$m_{salt\ 2}+dm_{salt\ 2}$	$m_{salt\ 3}+dm_{salt\ 3}$

Time t ***Time t + dt***

State 1 = .A mols NH_3 State 2 = .B mols NH_3 State 3 = .C mols NH_3

Define:

$dm_{salt\ 12}$ = mass converted State 1 to State2

$dm_{salt\ 23}$ = mass converted State 2 to State3

$dm_{gas\ 12}$ = mass of gas desorbed from State 1 to State2

$dm_{gas\ 23}$ = mass of gas desorbed from State 2 to State3

Use chemists' rate formula:

$$\frac{dX}{dt} = (1-X)^y A \frac{p_{eq} - p}{p}$$

assuming that converting phases unaffected by third phase, then:

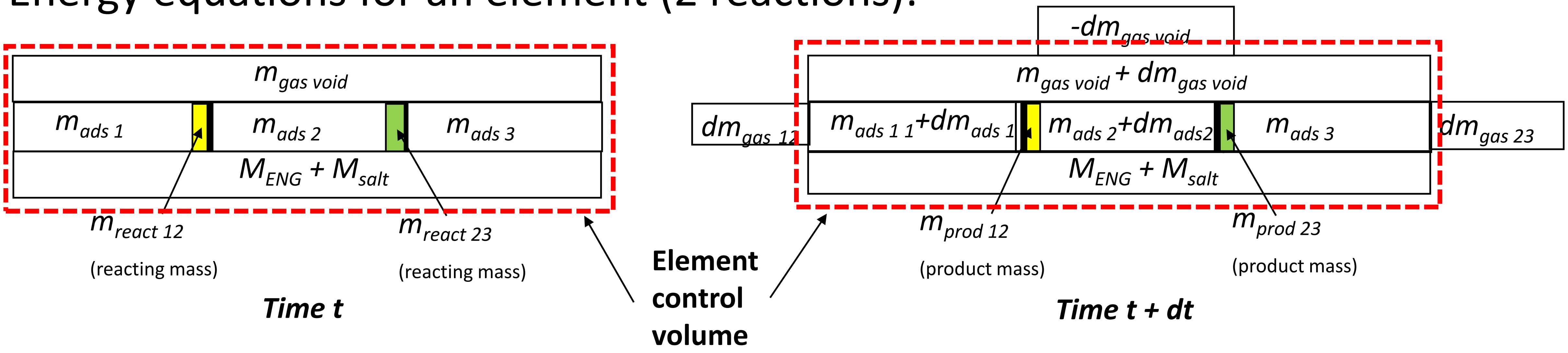
Reaction 12 (desorbing):

$$dm_{salt\ 12} = (m_{salt\ 1} + m_{salt\ 2})dt \left(\frac{m_{salt\ 1}}{m_{salt\ 1} + m_{salt\ 2}}\right)^{y_{12}} A_{12} \frac{p_{eq\ 12} - p}{p}$$

Reaction 23 (desorbing):

$$dm_{salt\ 23} = (m_{salt\ 2} + m_{salt\ 3})dt \left(\frac{m_{salt\ 2}}{m_{salt\ 2} + m_{salt\ 3}}\right)^{y_{23}} A_{23} \frac{p_{eq\ 23} - p}{p}$$

Energy equations for an element (2 reactions):



First Law for element control volume

$$dQ = \Delta U_{ENG} + \Delta U_{salt} + \Delta U_{ads} + \Delta U_{gas\ void} + dm_{gas\ 12} h_{out} + dm_{gas\ 23} h_{out} - dm_{gas\ void} h_{out}$$

[Desorption dm_{gas} is positive out and h_{out} is at element temperature

Adsorption dm_{gas} is negative and h_{out} is at reservoir temperature]

After much manipulation, for desorbing:

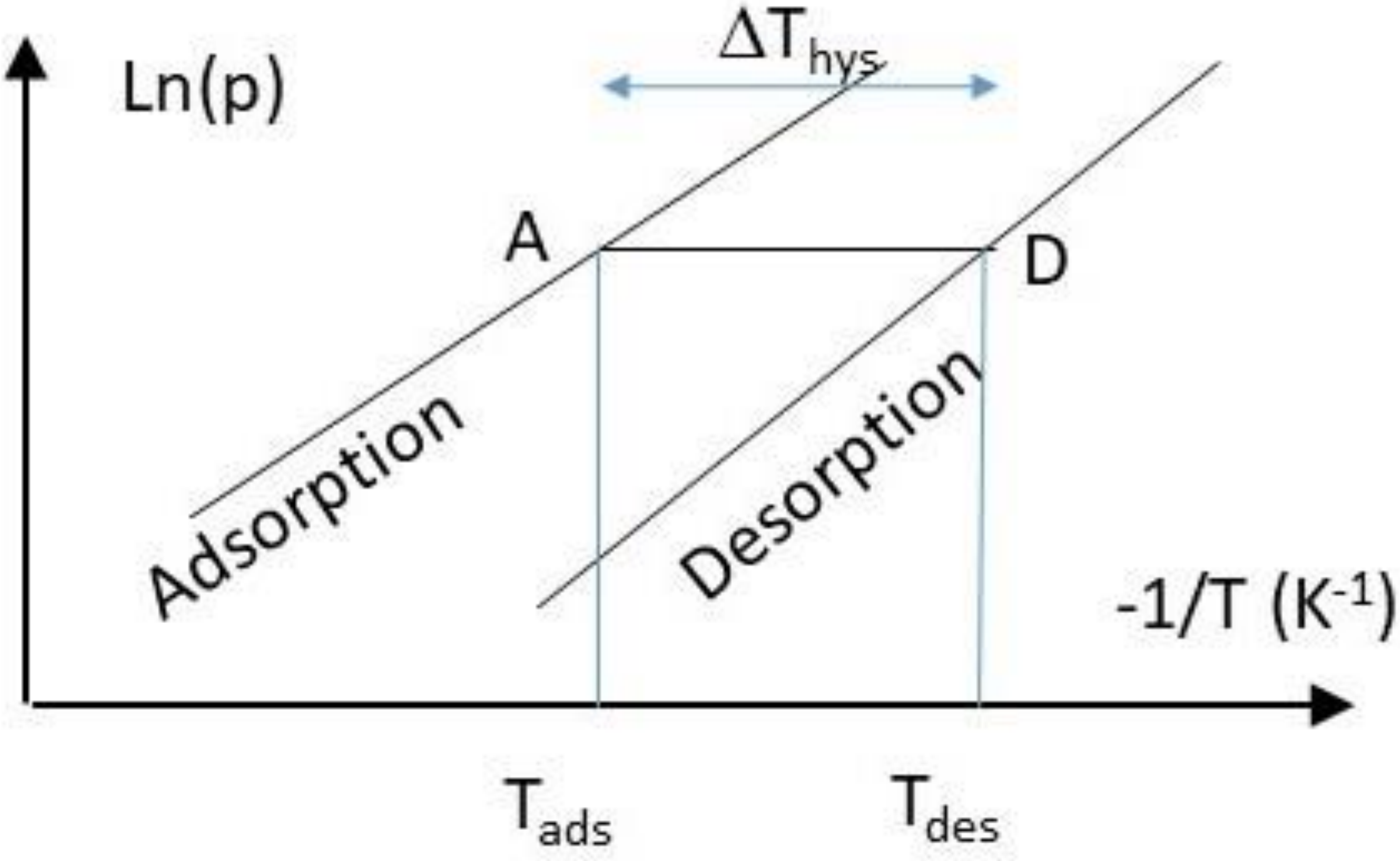
$$dT = \frac{dQ - dm_{gas\ 12}\Delta h_{12} - dm_{ads\ 12} p v_{ads}\left(1 - \frac{B}{A}\right) - dm_{gas\ 23}\Delta h_{23} - dm_{ads\ 23} p v_{ads}\left(1 - \frac{C}{B}\right) + V_{void}\frac{dp}{1 + dp/T}}{Mc_p + \sum_1^3 m_{ads}\, c_{v\ ads} + m_{gas\ void}\, c_{v\ gas} - V_{void}\frac{pT}{1 + dp/T}}$$

New Matlab code to handle complex models

```
% reactor_sim_1
% This is the top-level script file; everything else uses functions.

% User-edited code to set up
[rig, test] = rsim_parameter

% "rig" defines hardware, "t
% For traceability, both "ri
% in test,so to re-run the s
% rsim_parameters above and
% Both rig and test can be i

%----------------------------
% set derived values
rig = nodal_inputs(rig);
test
%---
test
```

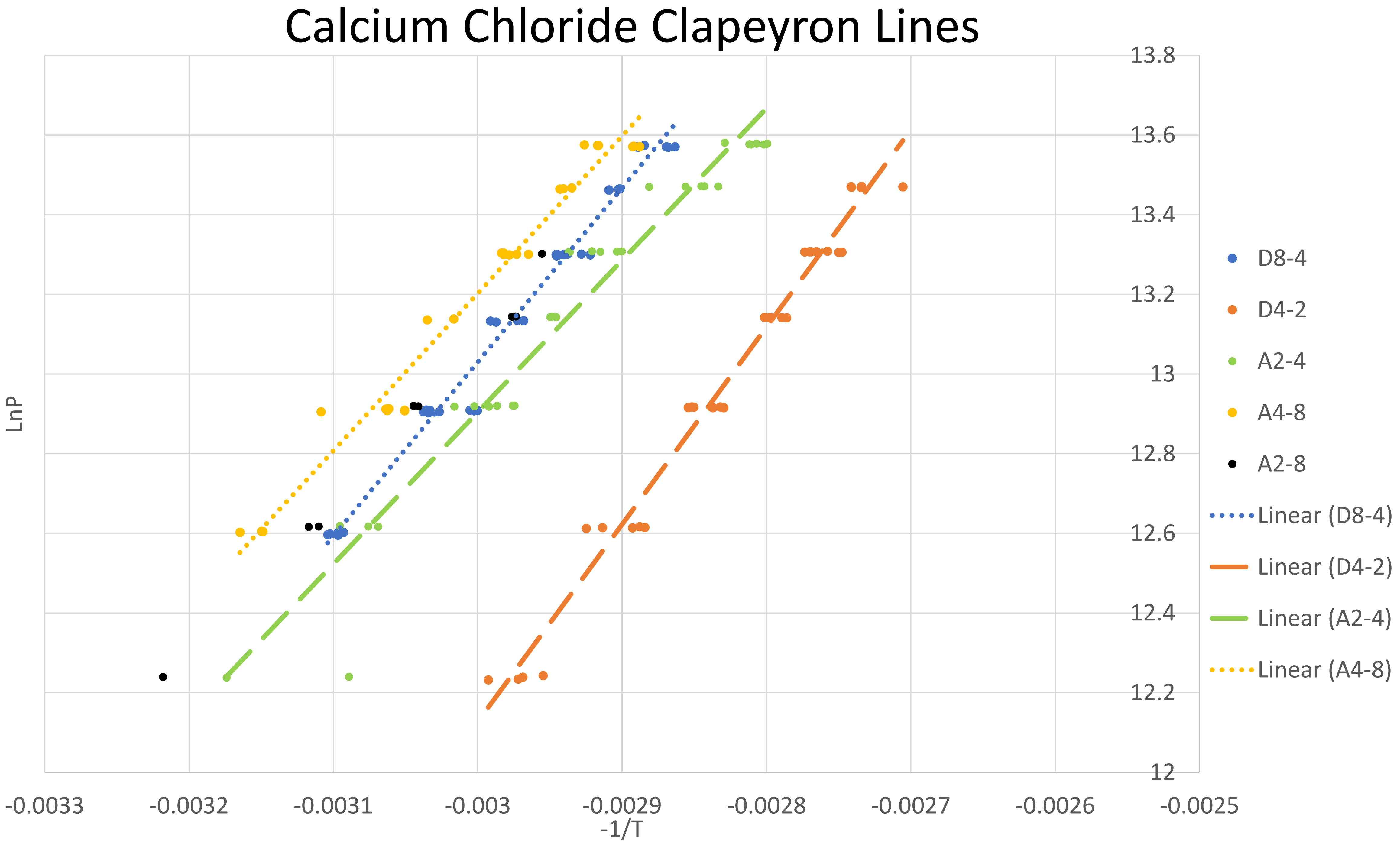
```
rig.Exp_vessel.mc = 4000;   % J/K
rig.Exp_vessel.vol = 0.002;   % m^3

rig.props.cvNH3ads = 3120; % J/kg NH3, guess???
rig.props.cpGas = 2760;   % J/kgK ammonia
rig.props.cENG = 720;   % J/kgK
.
.
iR = 1;
rig.Reactor(iR).gVol = 0.5E-3;   % m3
rig.Reactor(iR).iG = logical([0 1]); % gas to outside
rig.Reactor(iR).m = 0;   % linear
rig.Reactor(iR).mcp = 20e3;   % water pipe m*c
/mol of NH3 changing state, ads/des
J/molK ditto
```

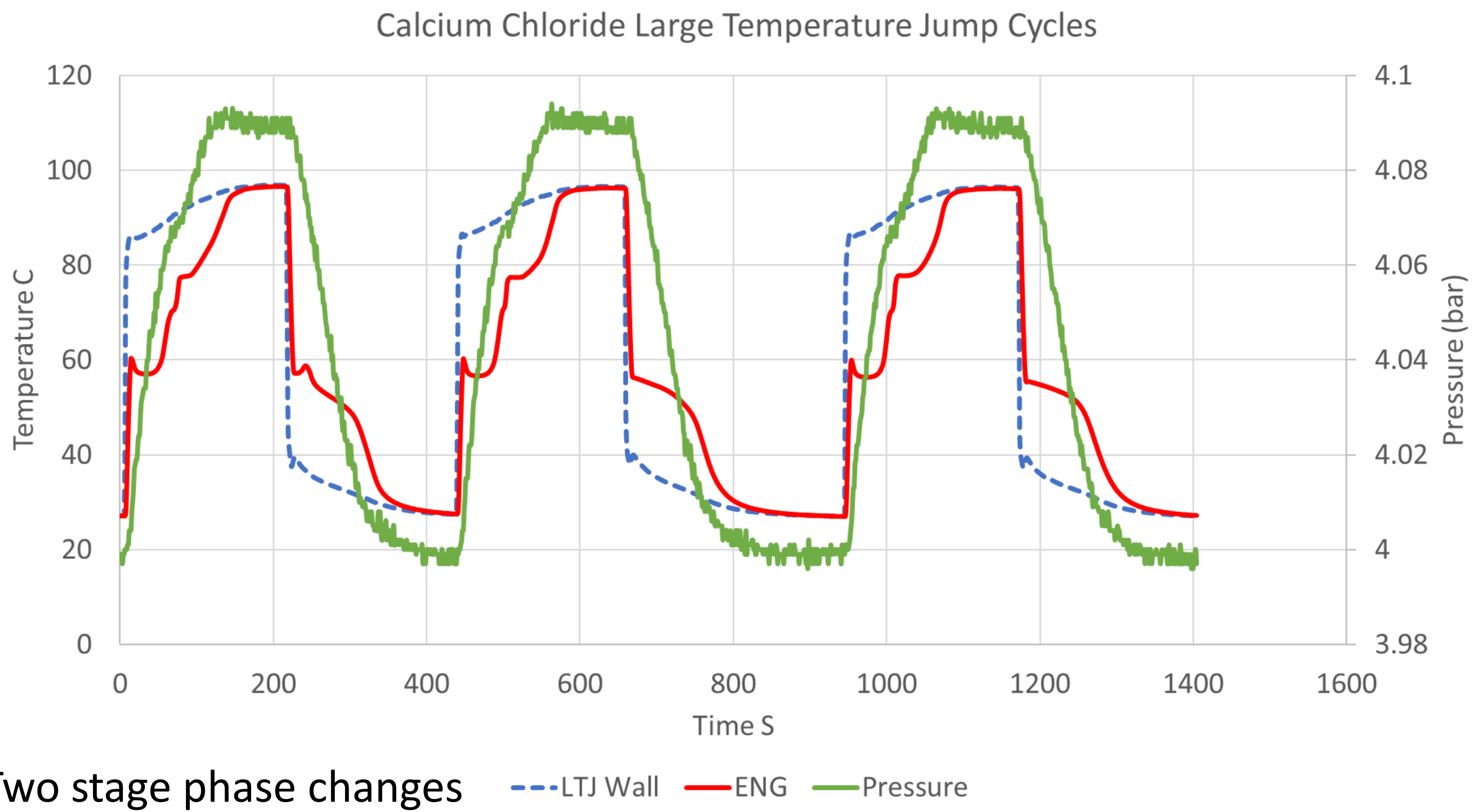
- Any number of reactors
- Any number of salts (assumed independent)
- Any number of reactions per salt
- 1D (x,t) flat or (r,t) cylindrical – could extend to 2D
- Allows non-uniform grids (Fornberg's algorithm)
- Uses Matlab's linked ODE solver for "Method of Lines" solution and structured variables for clarity



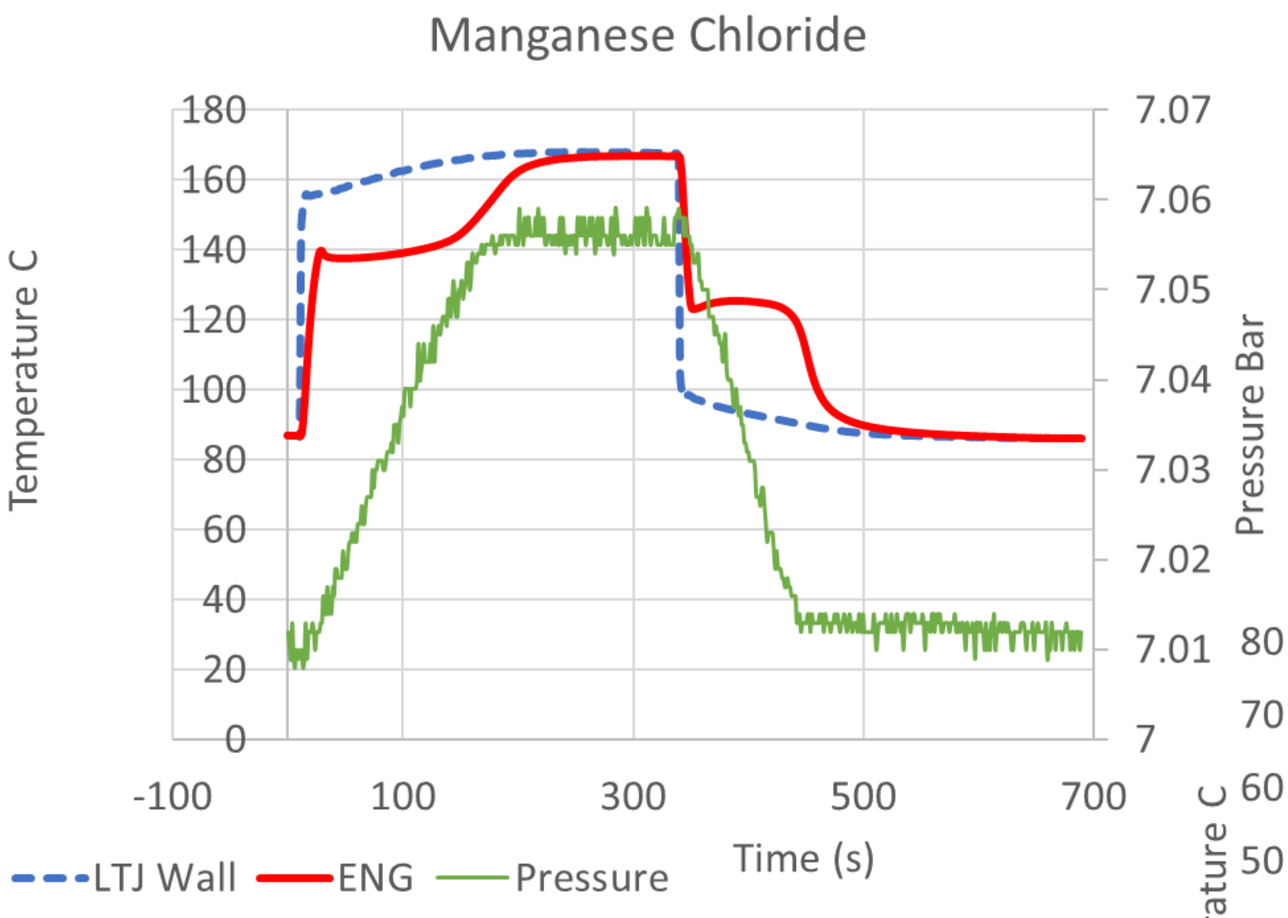
$$\Delta H_{ads} = \Delta H_{des} + \Delta T_{hys}\left(c_{v\,ads} - c_{v\,gas}\right)$$

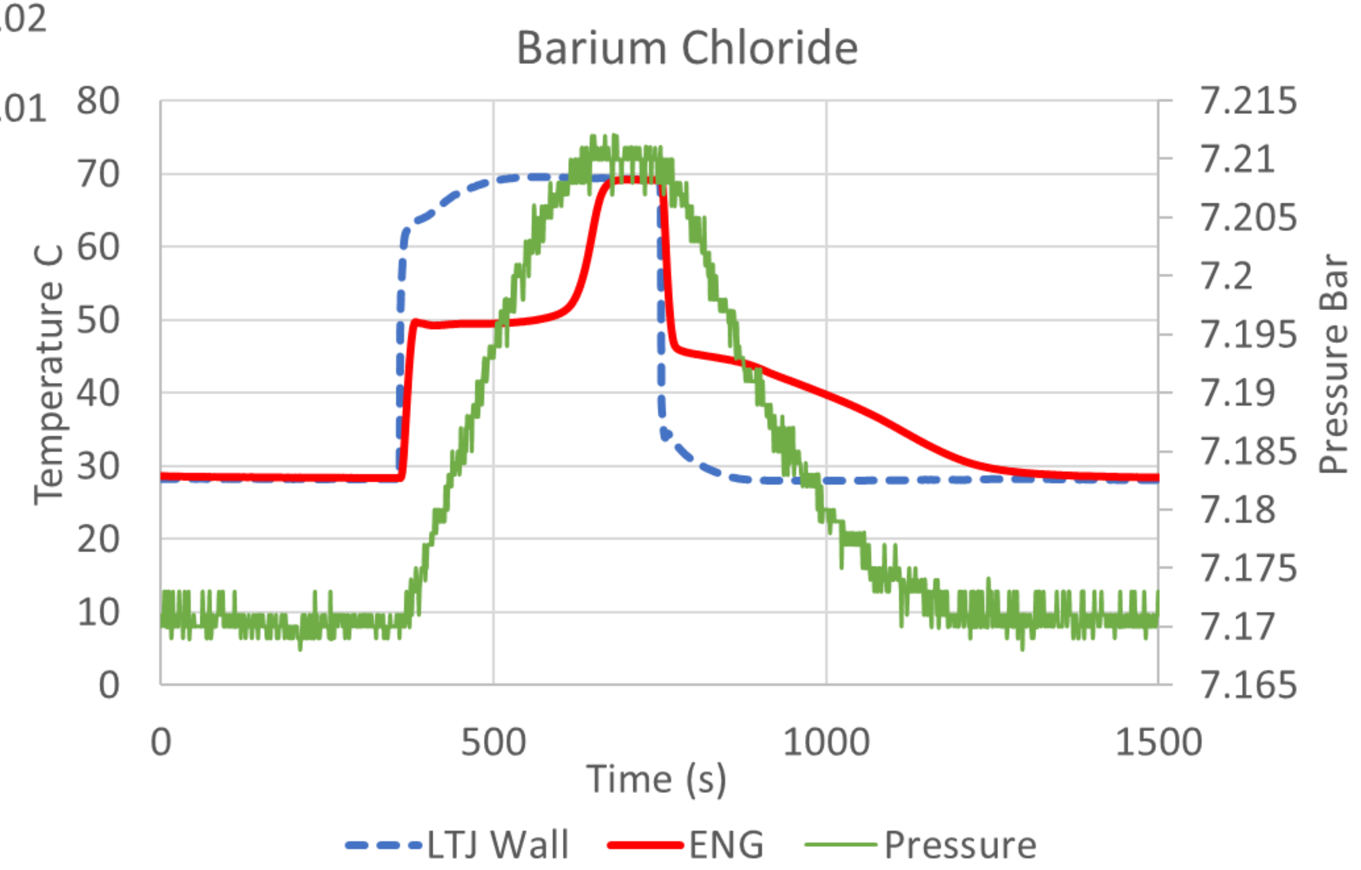
$$\boldsymbol{ln\left(p_{ads}\right) = \frac{\Delta S_{ads}}{R} - \frac{\Delta H_{ads}}{R\left(T_{des} - \Delta T_{hys}\right)}}$$


Calcium Chloride Clapeyron Lines
LnP
-1/T
13.8
13.6
13.4
13.2
13
12.8
12.6
12.4
12.2
12
-0.0033
-0.0032
-0.0031
-0.003
-0.0029
-0.0028
-0.0027
-0.0026
-0.0025
D8-4
D4-2
A2-4
A4-8
A2-8
Linear (D8-4)
Linear (D4-2)
Linear (A2-4)
Linear (A4-8)



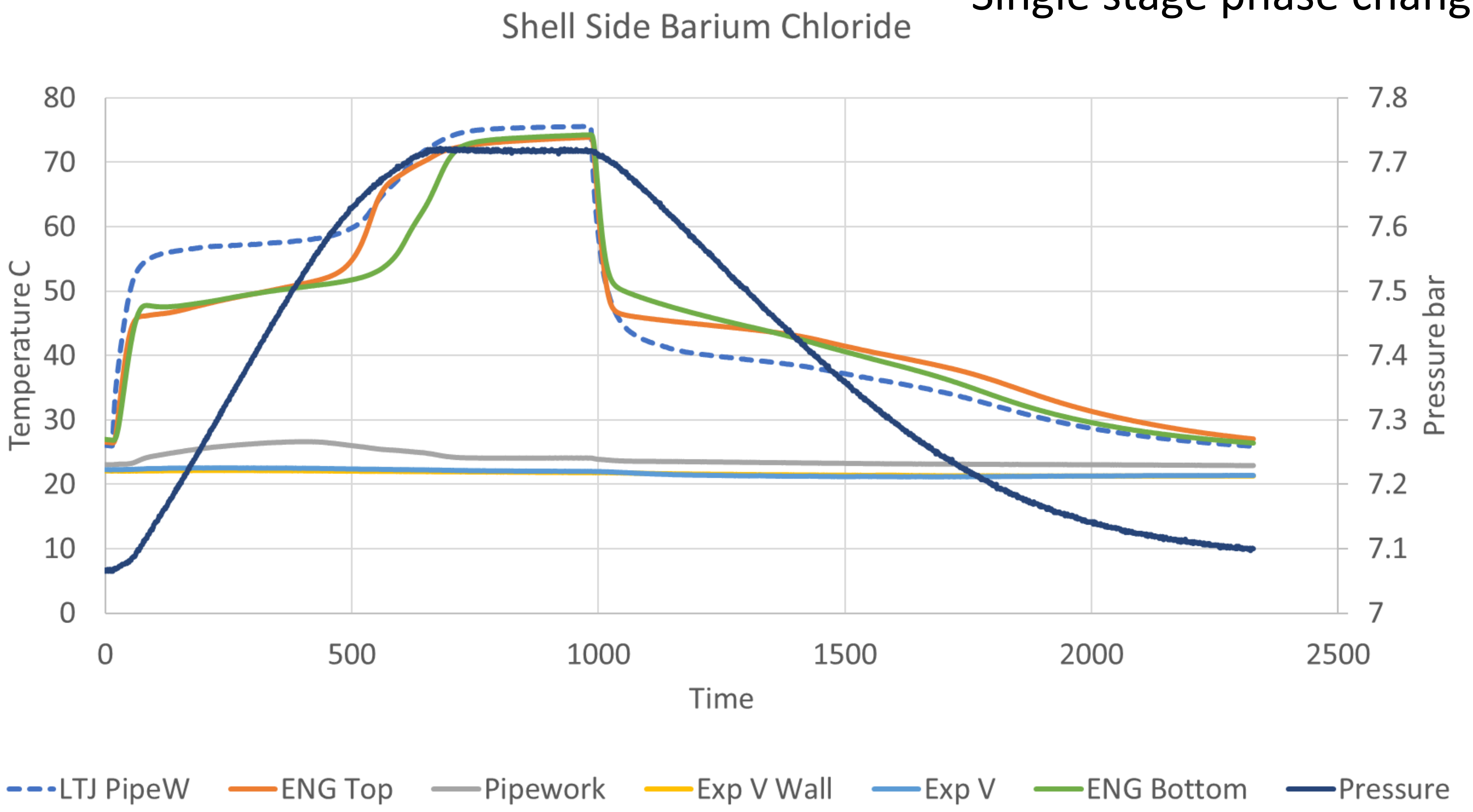
Two stage phase changes

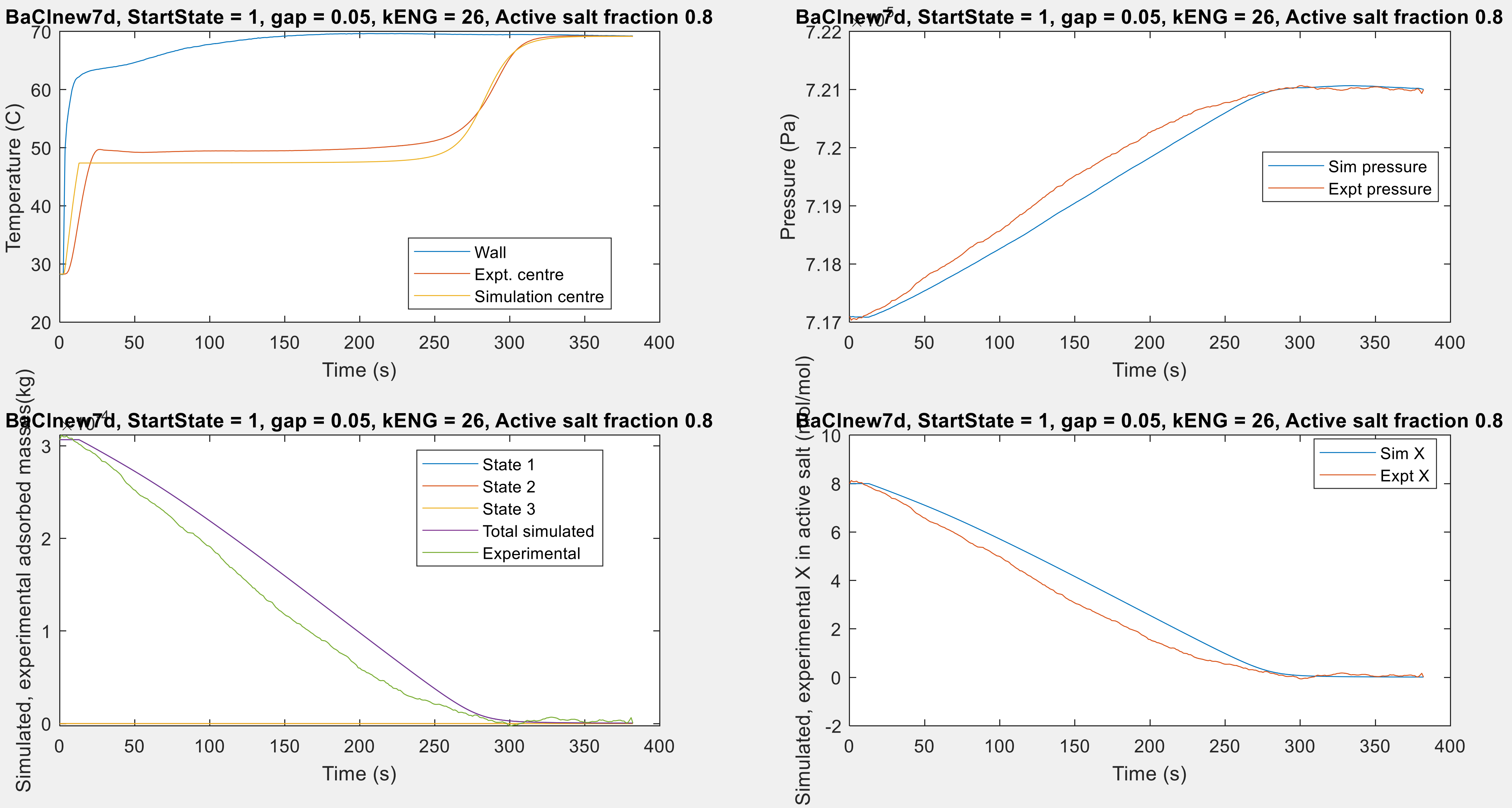


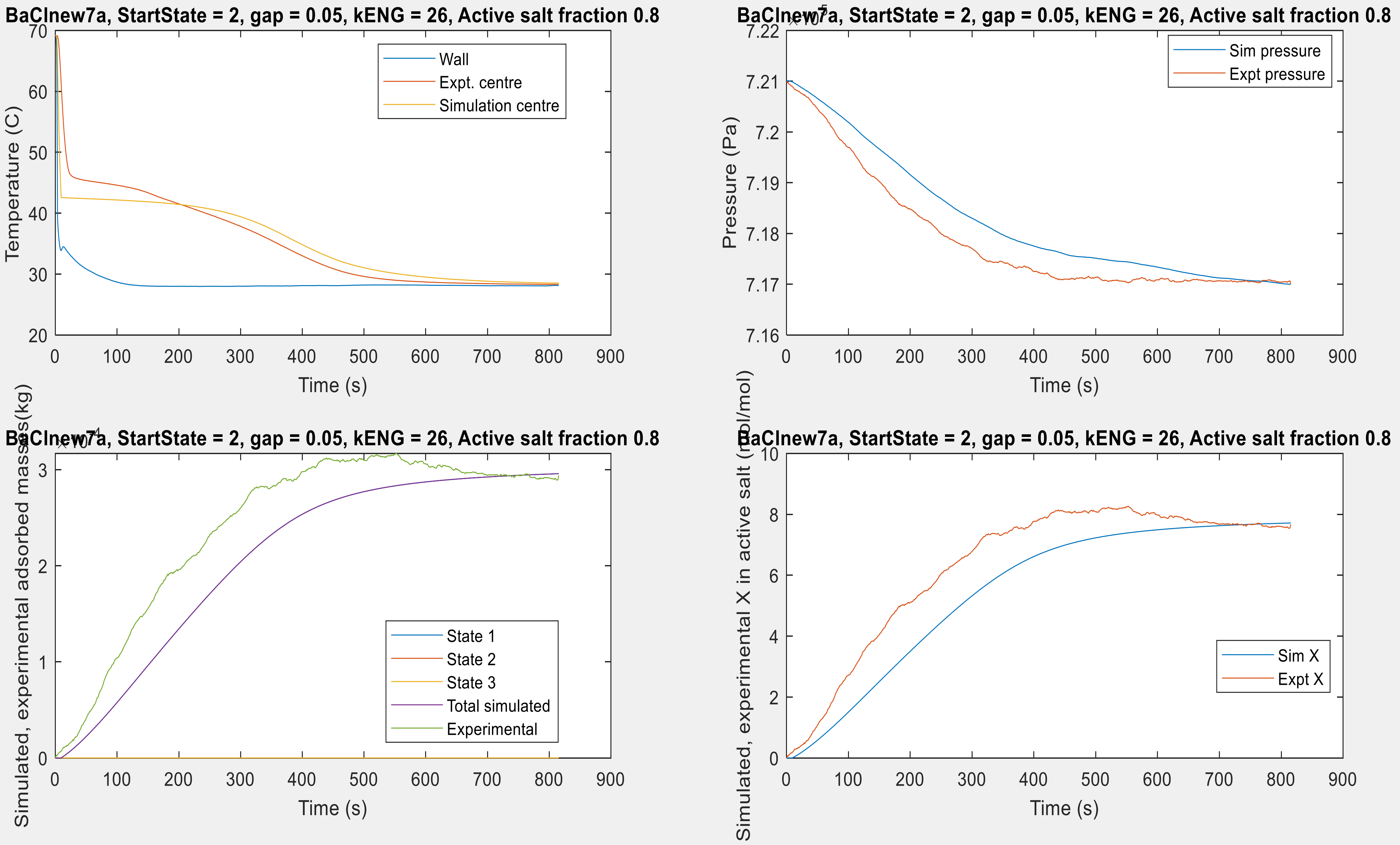


Single stage phase changes

Single stage phase change




BaClnew7d, StartState = 1, gap = 0.05, kENG = 26, Active salt fraction 0.8
Temperature (C)
Time (s)
Wall
Expt. centre
Simulation centre
BaClnew7d, StartState = 1, gap = 0.05, kENG = 26, Active salt fraction 0.8
× 10^5
Pressure (Pa)
Time (s)
Sim pressure
Expt pressure
BaClnew7d, StartState = 1, gap = 0.05, kENG = 26, Active salt fraction 0.8
× 10^-4
Simulated, experimental adsorbed mass (kg)
Time (s)
State 1
State 2
State 3
Total simulated
Experimental
BaClnew7d, StartState = 1, gap = 0.05, kENG = 26, Active salt fraction 0.8
Simulated, experimental X in active salt (mol/mol)
Time (s)
Sim X
Expt X


BaClnew7a, StartState = 2, gap = 0.05, kENG = 26, Active salt fraction 0.8
Temperature (C)
Time (s)
Wall
Expt. centre
Simulation centre
BaClnew7a, StartState = 2, gap = 0.05, kENG = 26, Active salt fraction 0.8
Pressure (Pa)
Time (s)
Sim pressure
Expt pressure
BaClnew7a, StartState = 2, gap = 0.05, kENG = 26, Active salt fraction 0.8
Simulated, experimental adsorbed masses(kg)
Time (s)
State 1
State 2
State 3
Total simulated
Experimental
BaClnew7a, StartState = 2, gap = 0.05, kENG = 26, Active salt fraction 0.8
Simulated, experimental X in active salt (mol/mol)
Time (s)
Sim X
Expt X

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Thank you for listening

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