Chemical Heat Pumps

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Heat Storage for Gen IV Reactors for Variable Electricity from Base-Load Reactors

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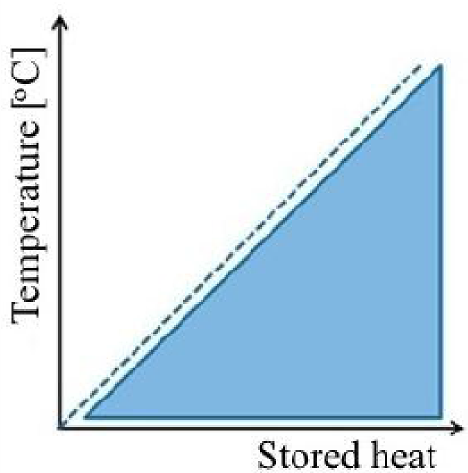
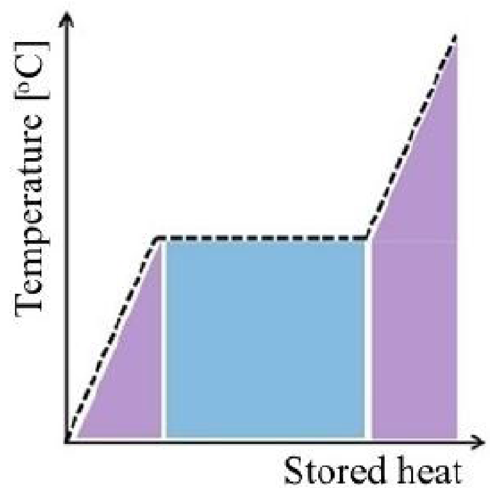
Contents

- Thermal Energy Storage Technologies
- Motivation: Industrial demand for elevated temperature heat supply
- Temperature Upgrading Technologies
- Working Pairs & CHP operating principles
- Temperature Amplification – Exothermic Hydration Process
- Advantages/disadvantages of CHPs
- Ongoing work and Future Direction

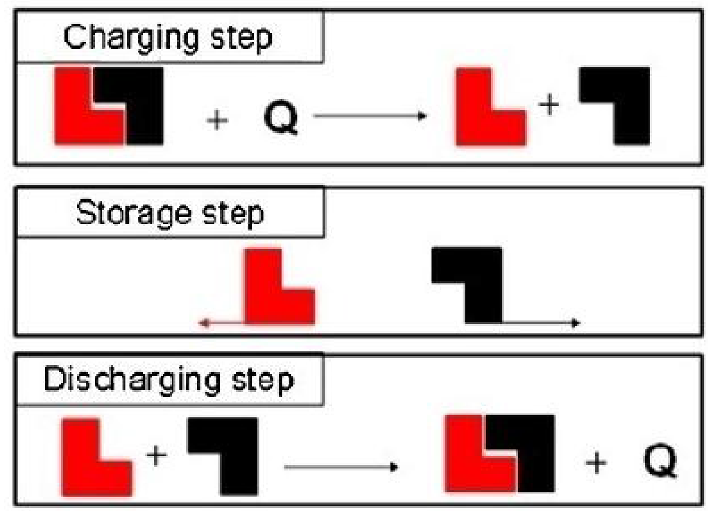
Thermal Energy Storage (TES) Technologies



Sensible Heat



Latent Heat



Thermochemical

Sarbu and Sebarchievici, *Sustainability*, **2018**, 10, 191

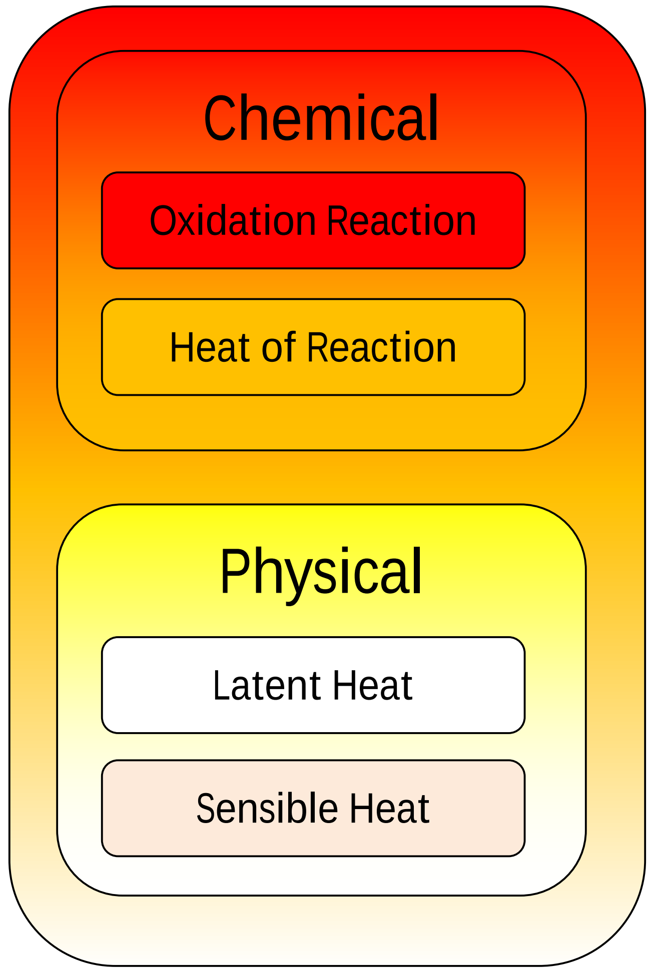
Comparison of TES Technologies

Characteristic	Sensible TES	Latent TES	TCS
Energy density	Low (0.2 GJ/m^3)	Medium (0.3-0.5 GJ/m^3)	High (0.5-3 GJ/m^3)
Heat loss	Significant heat loss over time	Significant heat loss over time	Small heat loss
Temperature range	Charging step temperature	Charging step temperature	Ambient temperature
Lifetime	Long	Limited	Depends on reactant degradation and side reactions
Transport	Small distance	Small distance	Unlimited theoretically
Advantages	Low cost and mature technology	Small volume and short distance transport possibility	High storage density, long distance transport possibility, low heat losses
Disadvantages	Significant heat loss over time; large volume needed	Small heat conductivity, materials corrosion, significant heat losses	Technically complex, high costs
Technical complexity	Simple	Medium	Complex

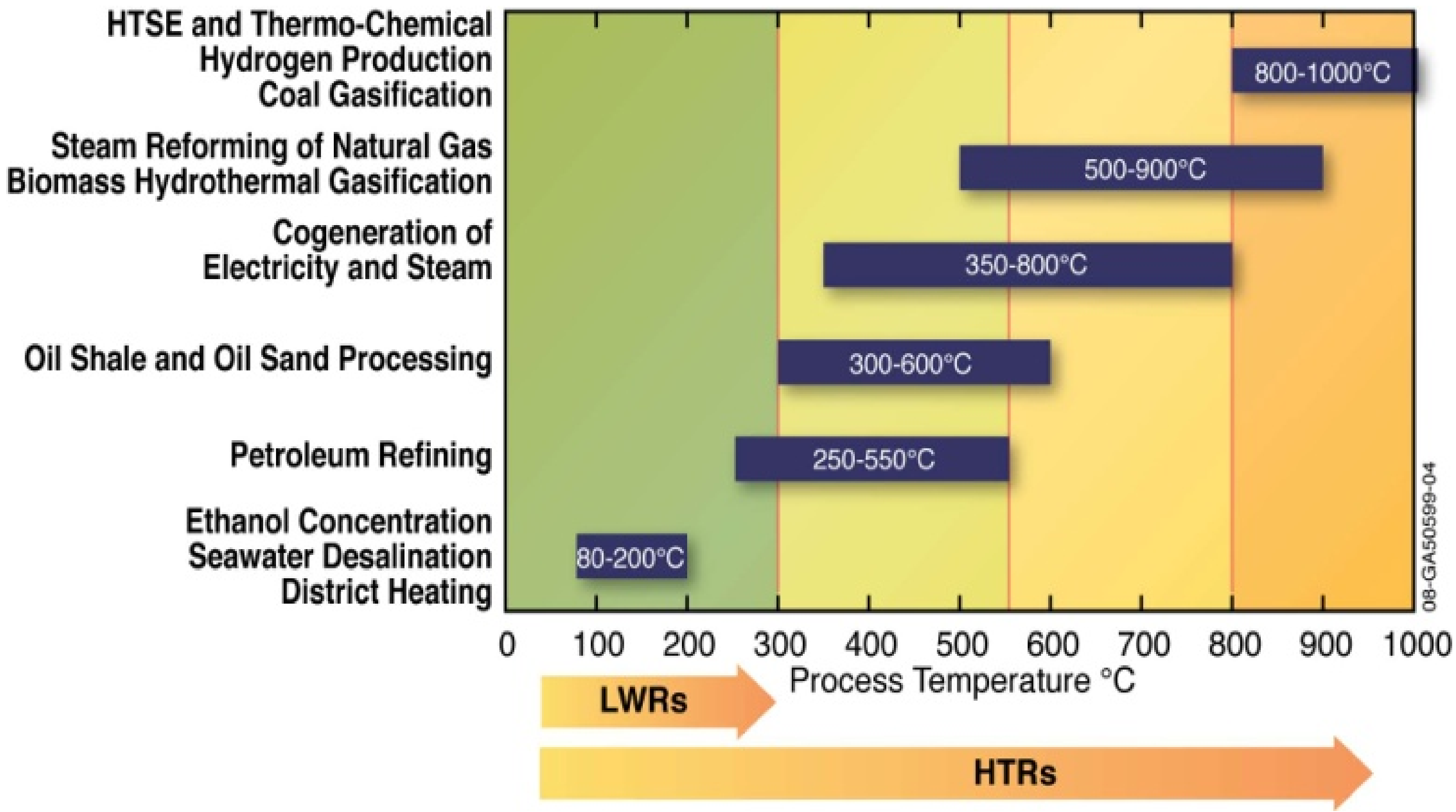
Liu et al, *Int. J. Energy Res.*, **2018**, 42, 4546

Energy Storage Density Diagram

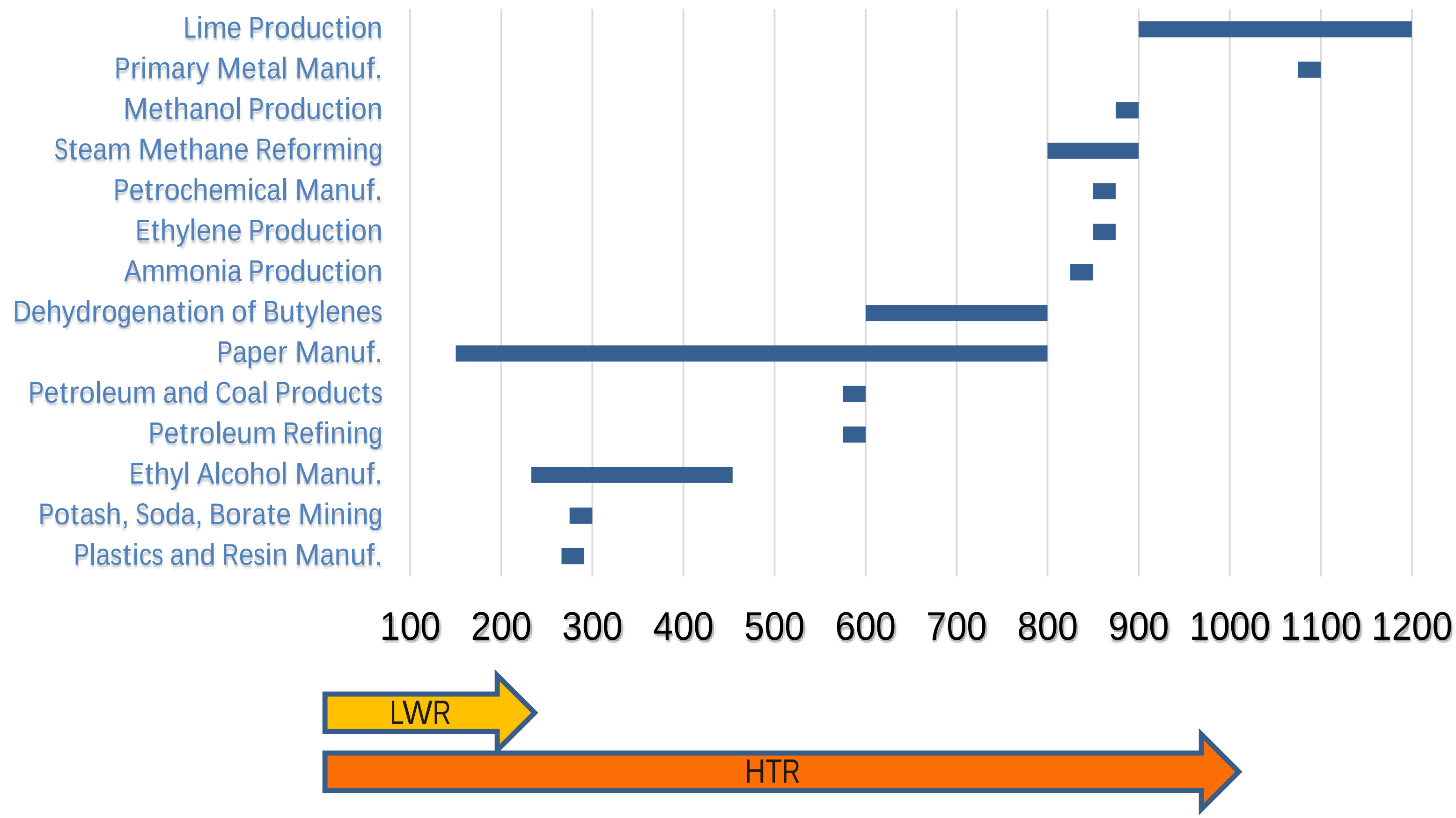
Sensible heat < latent heat < chemical reaction < oxidation reaction



Process Heat Applications



Process Heat Applications



McMillan *et al.*, 2016, NREL/TP-6A50-66763

Motivation

In order to realize the benefits of nuclear hybrid energy systems with the current LWR reactor fleets, selection and development of a complimentary temperature upgrading technology is necessary

- Potential of production of synthetic fuels based on indigenous carbon sources using nuclear energy
- Process temperature requirements: pyrolysis and hydrotreatment/hydrocracking – 500^{o}C; gasification and reforming – 800^{o}C
- Conventional LWRs outlet temperatures:~300°C

Technology Requirements and Selection for LWR Temperature Upgrading

- Ability to upgrade LWR outlet temperature to levels required for process heat applications (500-800°C)
- Ability to integrate with nuclear hybrid energy systems (tolerant of dynamic or transient operation)
- Economic viability, reliability, and operational safety
- Direct utilization of LWR heat with minimal energy conversion steps

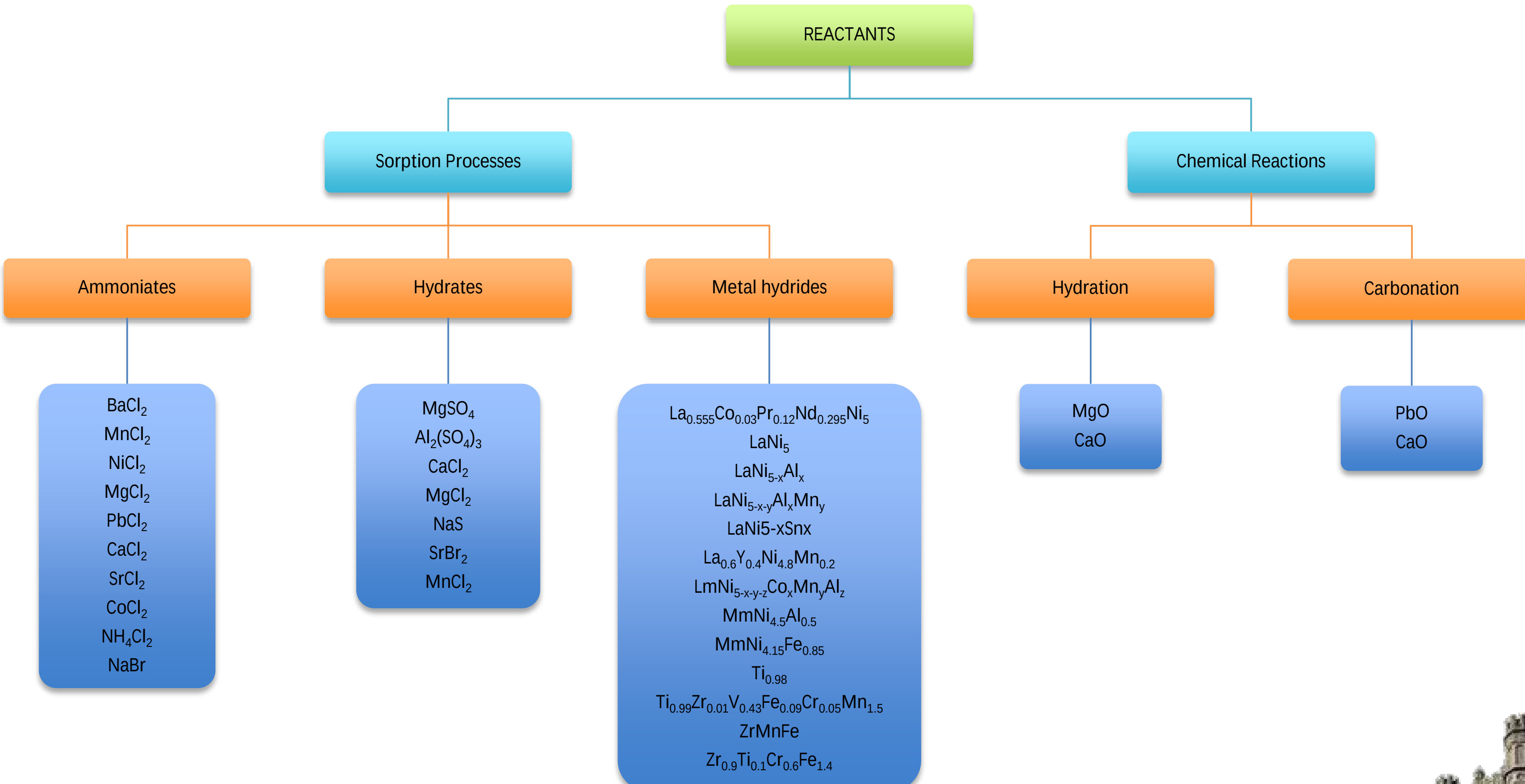
Temperature Upgrading Technologies

- Mechanical Heat Pumps
  - Reverse power cycle (Rankine, Brayton)
  - Low temperature upgrade (up to 200°C)
  - Requires mechanical power source
- Vapor Absorption Heat Pumps
  - Low temperature upgrade (up to 260°C)
  - Driven by thermal energy sources
  - Higher efficiency with few moving parts
- Solid State Heat Pumps
  - Use magnetic or thermoelectric effects to achieve thermal energy transport
  - Require electrical power input
  - Best suited for refrigeration and space heating and cooling applications
- Chemical Heat Pumps (CHPs)
  - Use reversible chemical reactions to change the temperature level of the thermal energy stored by the chemicals
  - High temperature upgrade possible

Chemical Heat Pump Types

- Sorption processes
  - Heating and cooling applications
  - Heat and mass transfer limitations
  - Relatively low temperature (range)
- Chemical reactions
  - Heating and cooling applications
  - Heat and mass transfer limitations
  - Storage of medium and high grade heat (>400°C)

Overview of working pairs



Cot-Gores et al, *Renewable Sustainable Energy Rev.*, **2012**, 16, 5207

Advantages of CHPs

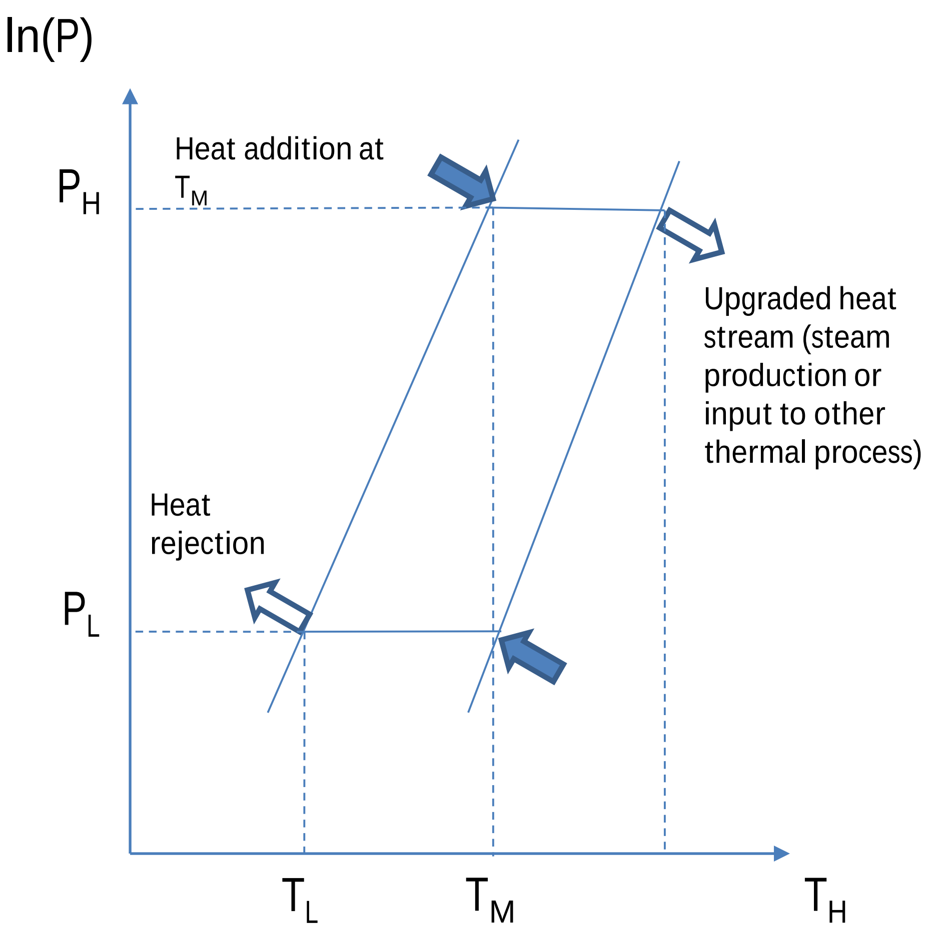
- Operating temperature range higher than mechanical heat pumps
- Reversible reactions (oxidation reactions have higher energy density but are irreversible)
- Possible to operate without mechanical energy input (Hasatani 1992)
- Energy storage potential
  - High energy density relative to sensible or latent heat storage (large energy storage per unit mass)
  - Energy storage without heat loss as in case of sensible or latent heat storage (no insulation required as energy is stored as chemical potential energy)
  - Potential to operate with thermal energy at various temperatures (Hasatani 1992)
- Reaction materials metal oxides/carbonates tend to be inexpensive and non-toxic

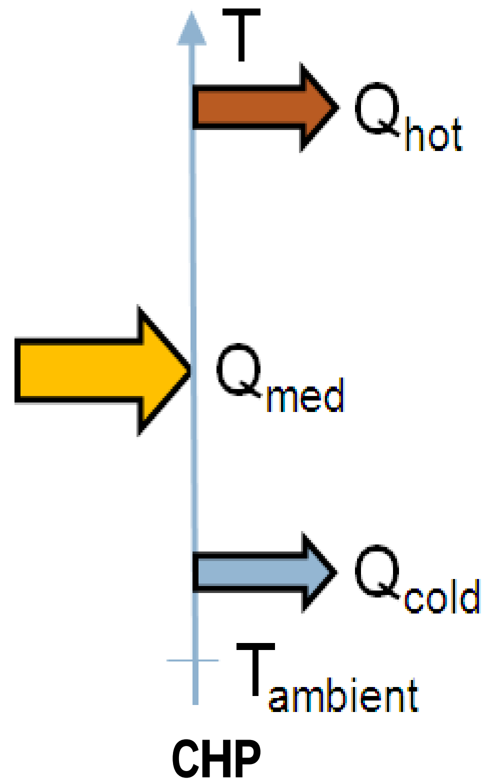
Hasatani M. (1992). Highly developed energy utilization by use of chemical heat pump. In Global Environmental Protection Strategy Through Thermal Engineering, Hemisphere Publishing, New York, pp. 313-322.

Disadvantages/Issues

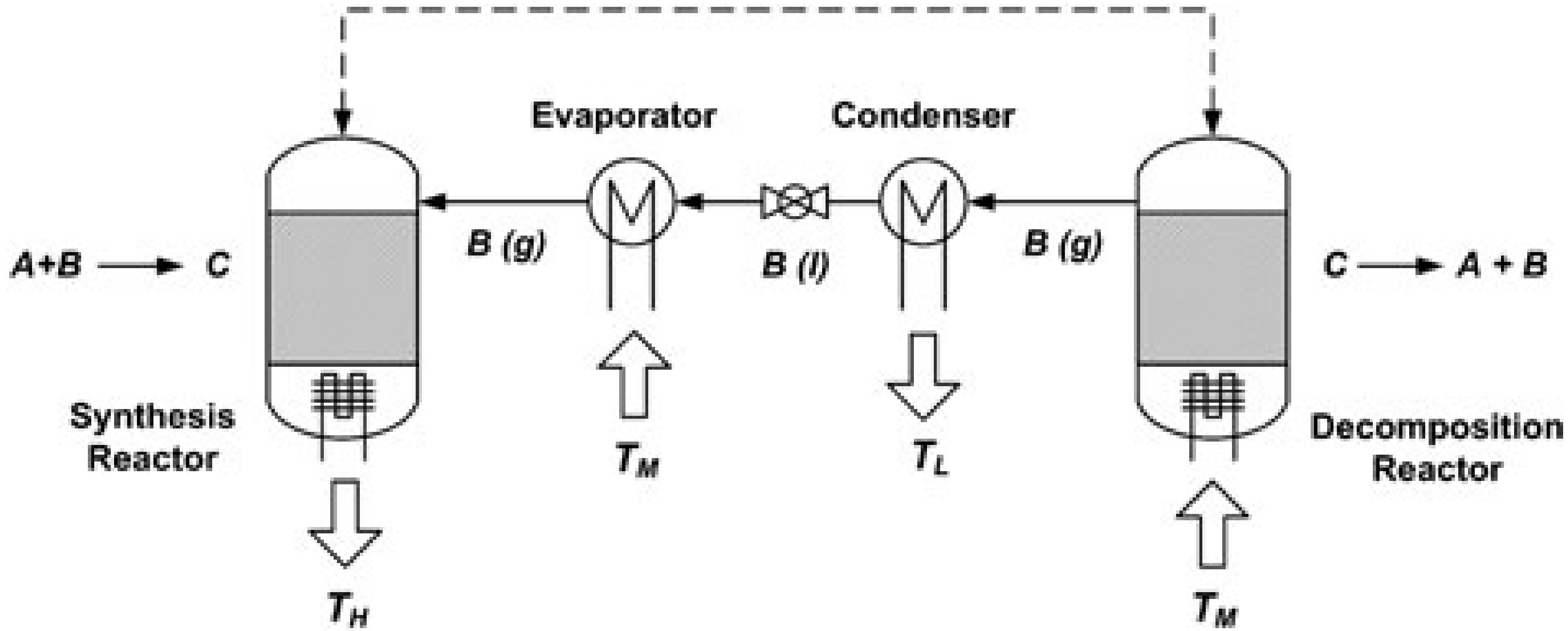
- Inorganic solid/gas CHPs operate as batch processes
- Heat transfer limitations associated with packed bed reactors and solid/gas phase reactions
- Materials stability and durability issues
- Transient systems with temperature fluctuations leading to generation of thermodynamic irreversibility

CHP Operation





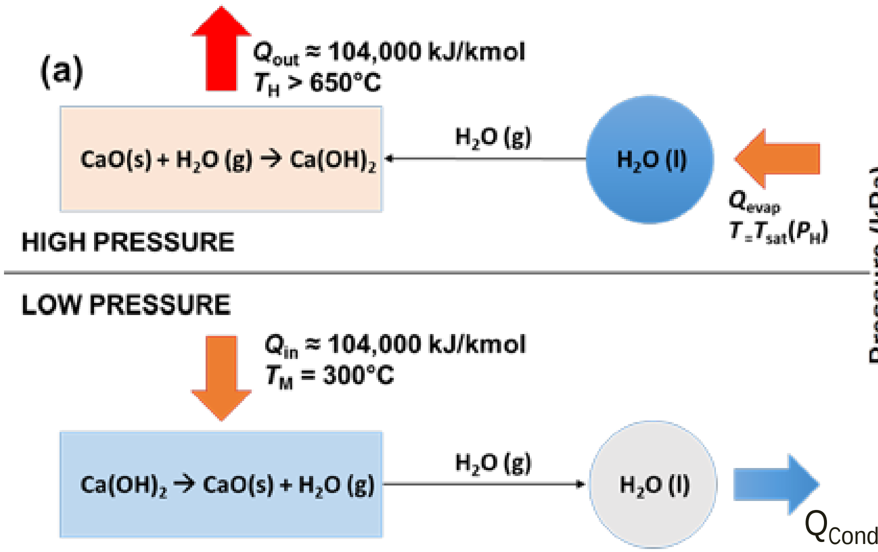
For Continuous Operation: Multiple Reactors



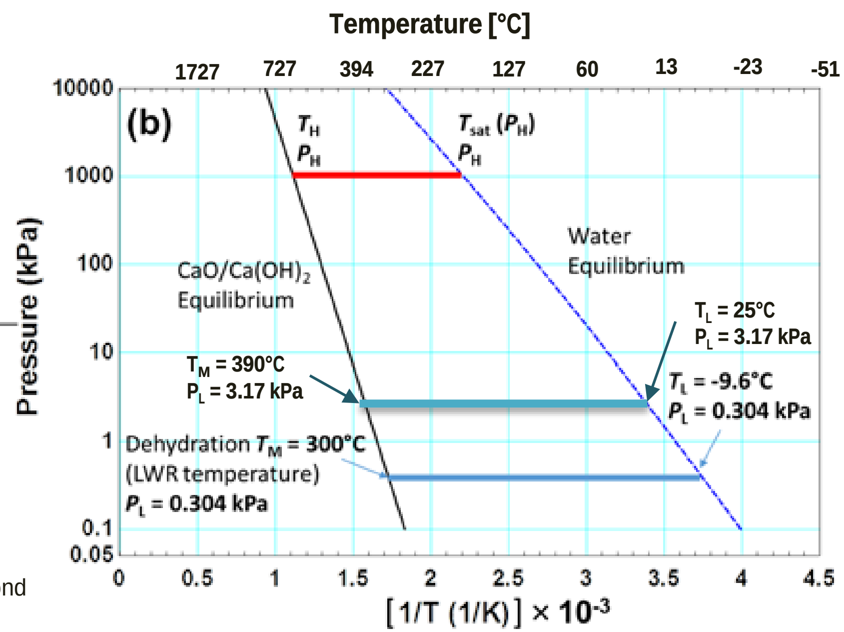
More reactors could also provide sensible heat recuperation to improve heat integration, reducing the thermodynamic losses.

Arjmand et al, *Int. J. Energy Res.*, **2013**, 37, 1122

Dehydration-Hydration CHP

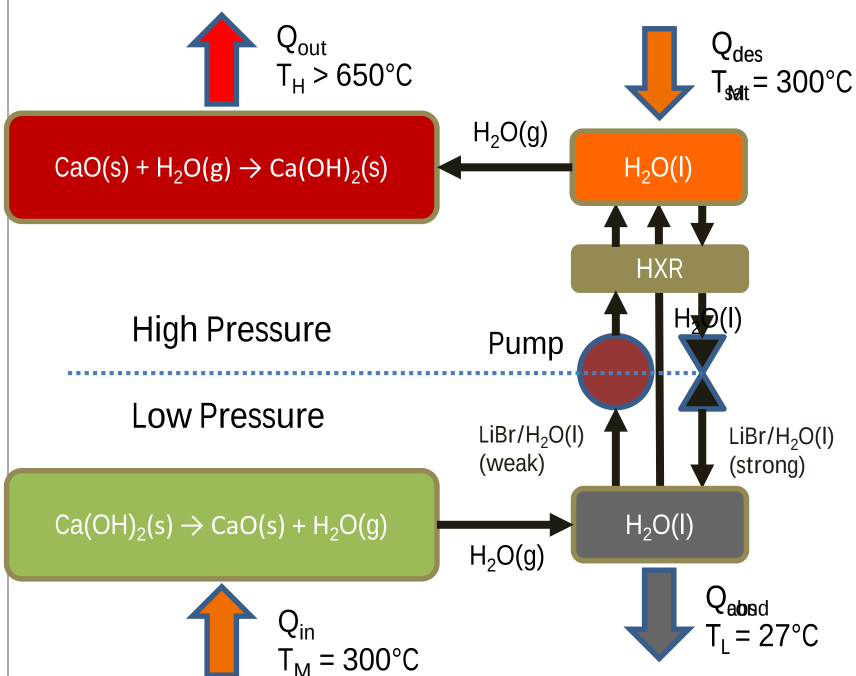


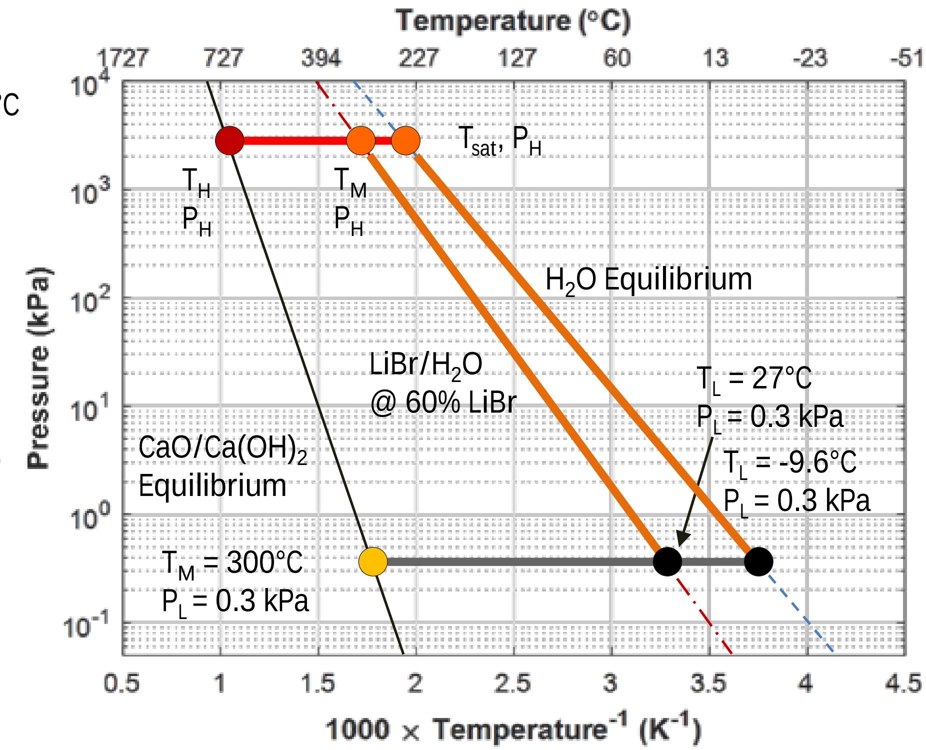
Schematics of component of CHP system



Heat pump cycle on Clausius-Clapeyron diagram showing equilibrium of $CaO/Ca(OH)_2$ and $H_2O_{(L)}/H_2O_{(G)}$

Chemical/Absorption Heat Pump

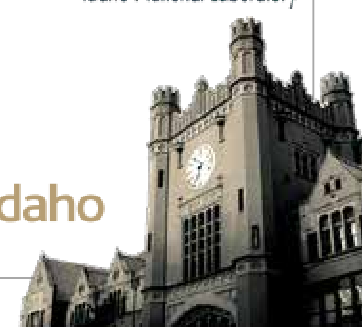




Sabharwall *et al.*, 2013

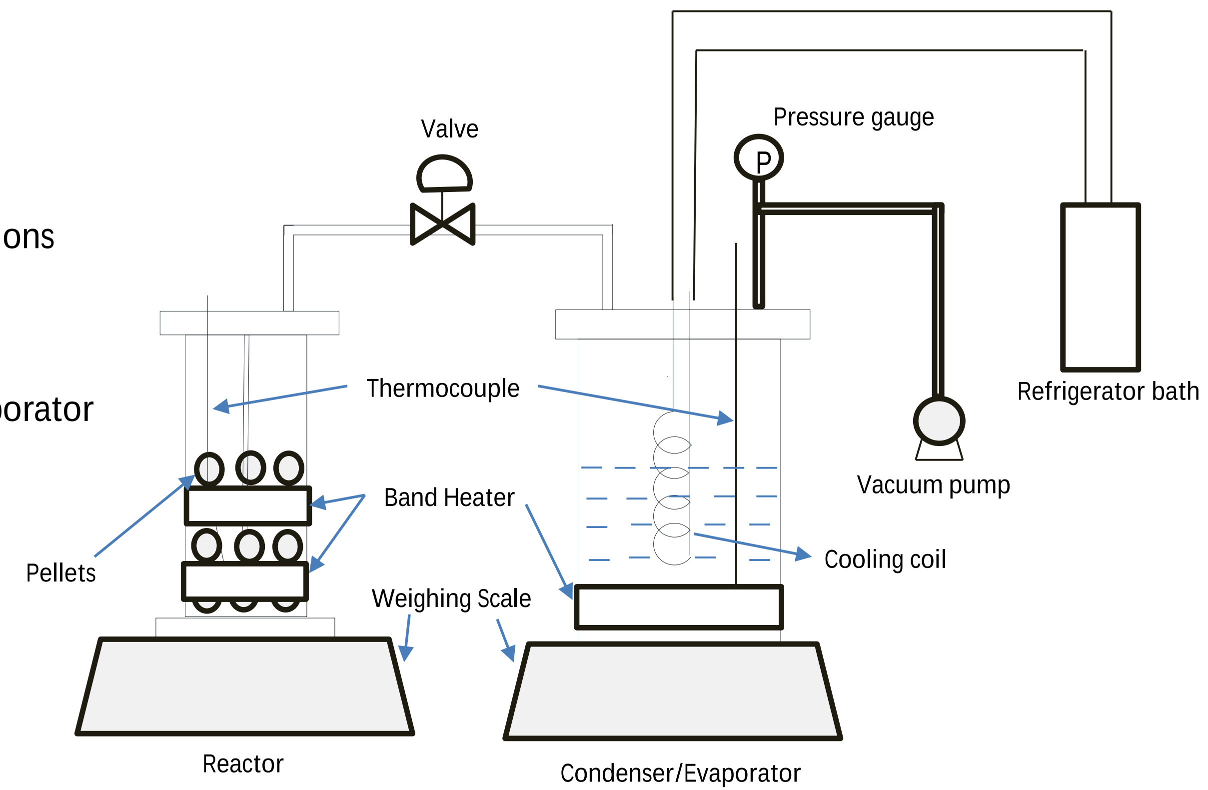
Research Effort and Collaboration

- University of Idaho
  - Transient heat and mass transfer and reaction kinetics of CaO
  - Material characterization of CaO
- Oregon State University
  - Transient high temperature heat pump performance
  - Model and evaluate entire system
  - Design, build, and test absorption heat pump subsystem
- Idaho National Laboratory
  - Facilitate university collaboration
  - Enable system integration tests



Materials and Methods

- Reactor Dimensions
  ID – 2.5”
  Height – 9”
- Condenser/Evaporator Dimensions
  ID – 4.4”
  Height – 8”



Materials and Methods

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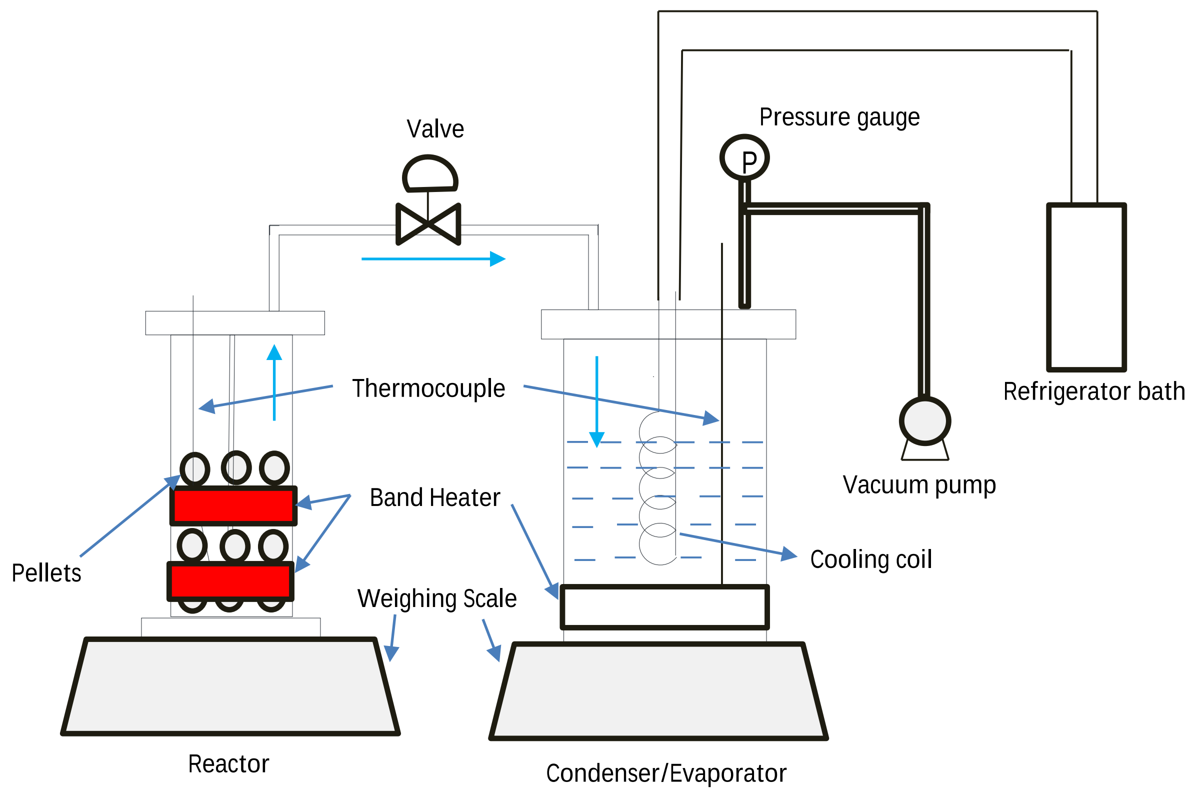

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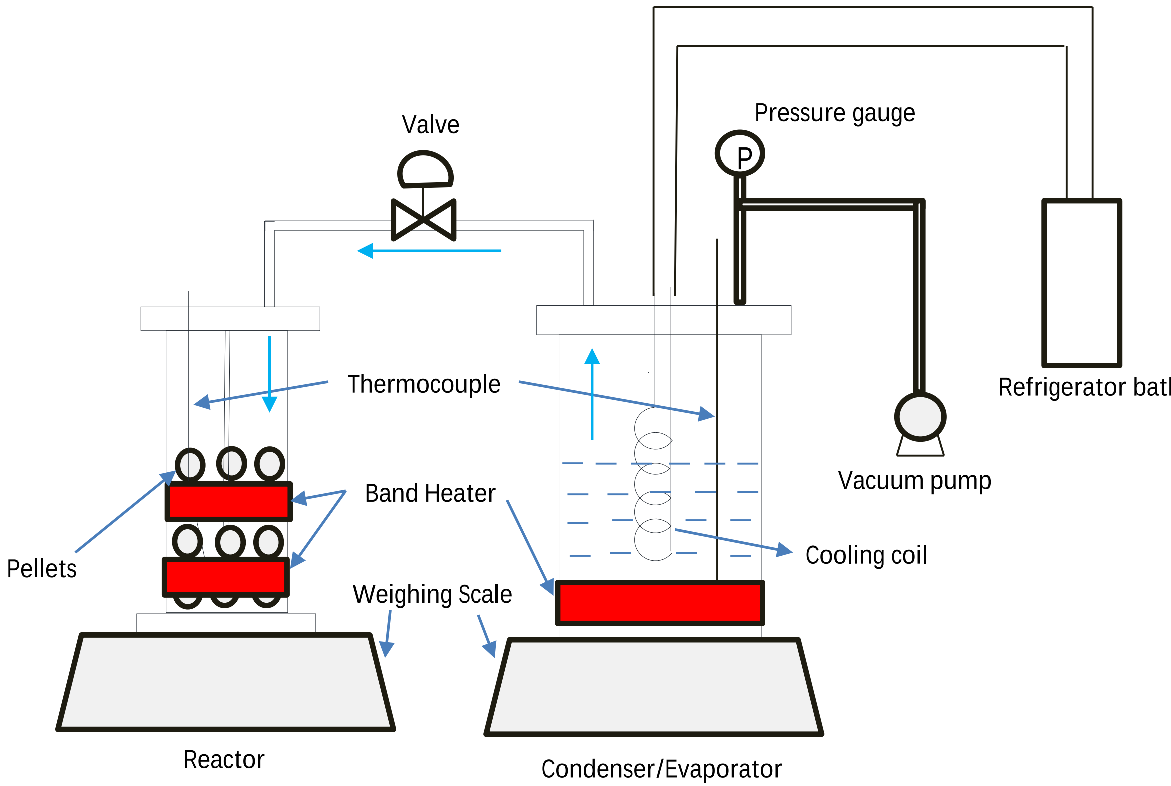


Figure 7 : Schematic of Experimental Setup

Preliminary Results

TABLE III. Change in the reading of weighing scale and unconverted mole fraction with time during dehydration process

Time (min)	Weighing Scale Reading (g)		Unconverted mole fraction
	Reactor	Condenser	
0	0	0	0
118	-3	2	0.95
120	-8	7	0.88
124	-15	13	0.78
126	-30	28	0.57
128	-34	32	0.51
132	-51	48	0.27
135	-60	57	0.14
140	-68	64	0.03

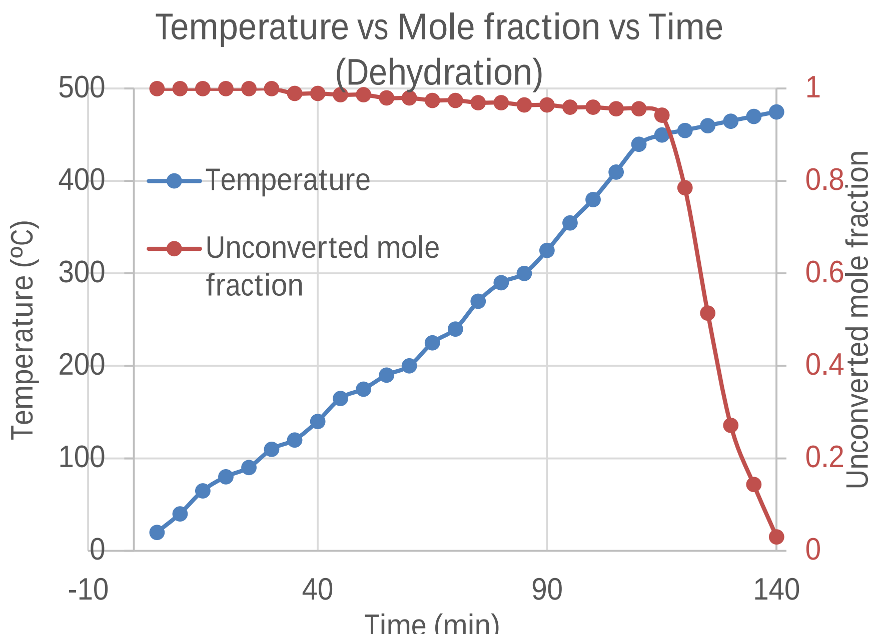
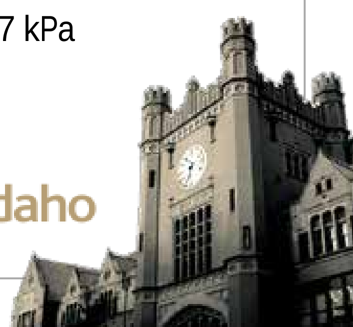


Figure 8 : Temperatures and unconverted mole fraction during dehydration reaction P = 3.17 kPa



Preliminary Results

- Hydration

$CaO(s) + H_2O(g) \leftrightharpoons Ca(OH)_2(s) + \Delta\hat{H}_r$ $\Delta\hat{H}_r = 104.4$ kJ mol^{-1}

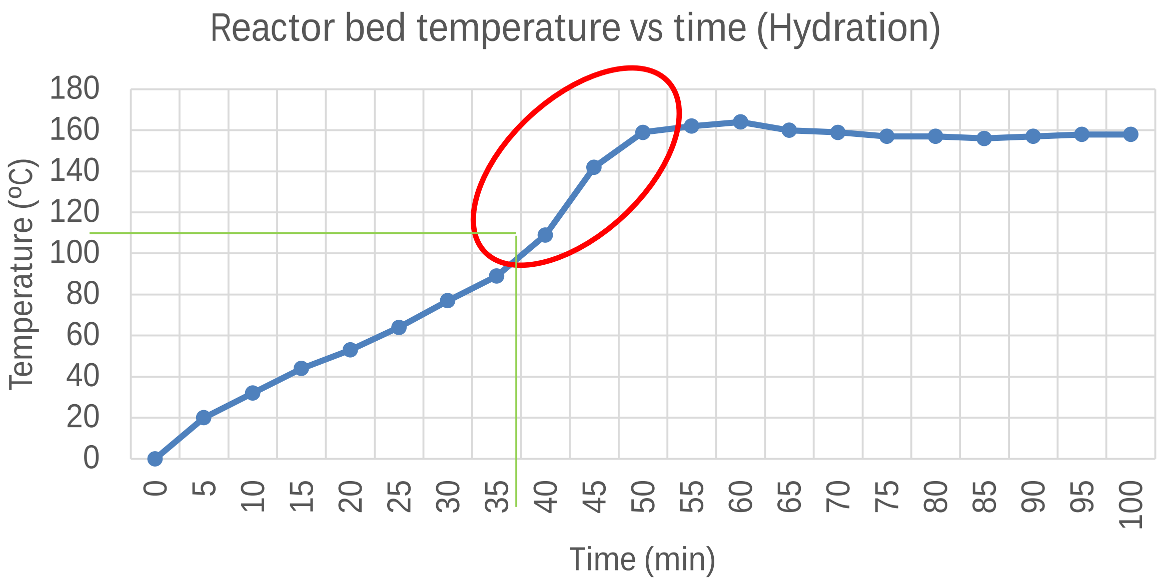


Figure 10 : Temperature profile during hydration process

Observations and Conclusions

- Dehydration process
  - Nearly complete decomposition of $Ca(OH)_2$ in ~150 min
- Hydration process
  - Temperature increase due to exothermic recombination of CaO and H_2O observed
- Absorber-Desorber Modeling
  - Thermal pathway increases exergetic efficiency to >80%
  - Absorber inlet conditions greatly impact performance

Future Work

- Experimental investigation of performance change for repeated dehydration/hydration cycles
- Validation of experimental data with theoretical analysis
- Dynamic chemical/absorption heat pump model development
- Experimental investigations of absorber-desorber system

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Nuclear Energy University Program

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