Brandenburg
University of Technology
Cottbus - Senftenberg

Thermal Energy Storage Systems Engineering

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Institute of Process and Material Sciences

Seminar - Energy Systems Initiative at CAPD, **December 04, 2023**

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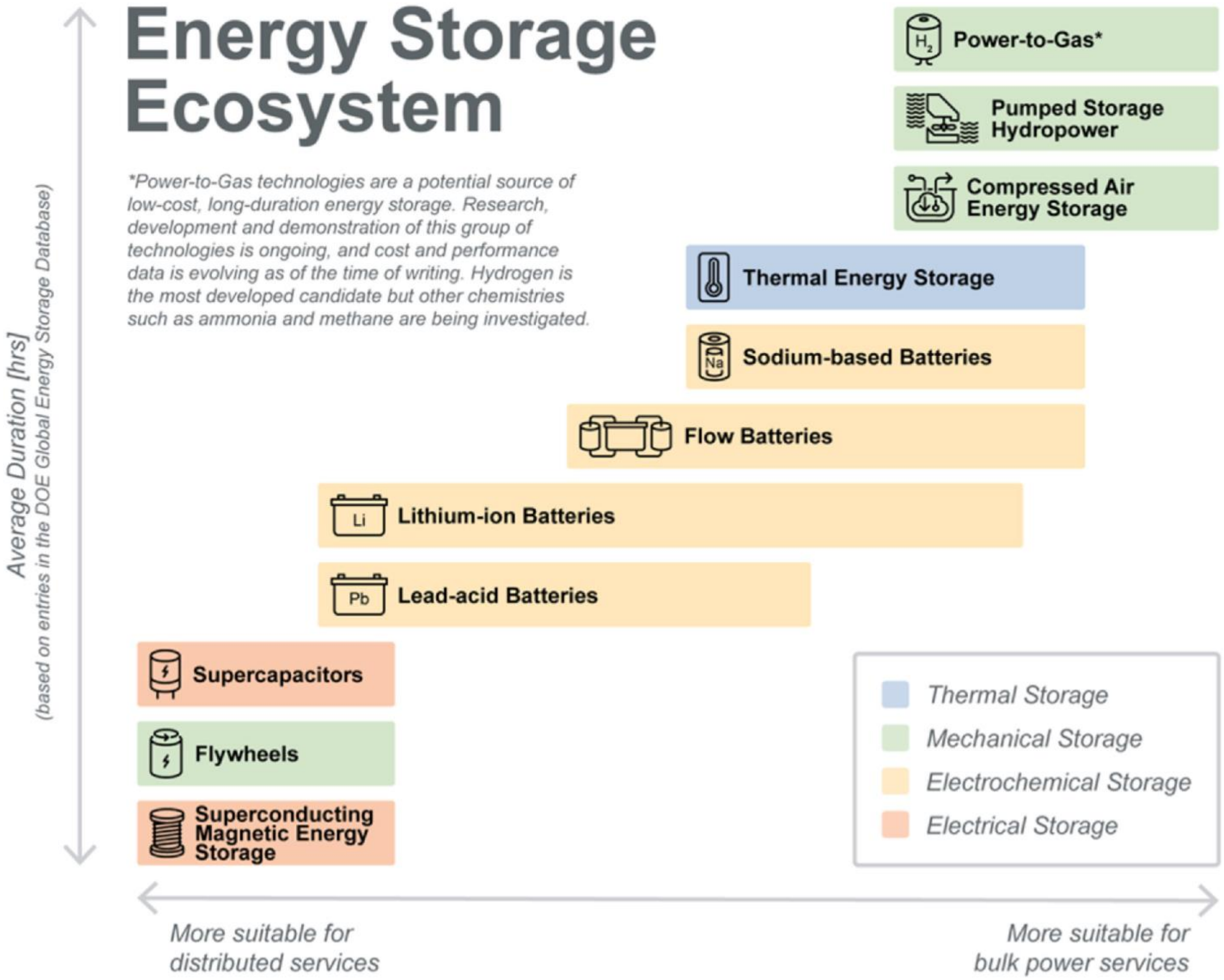
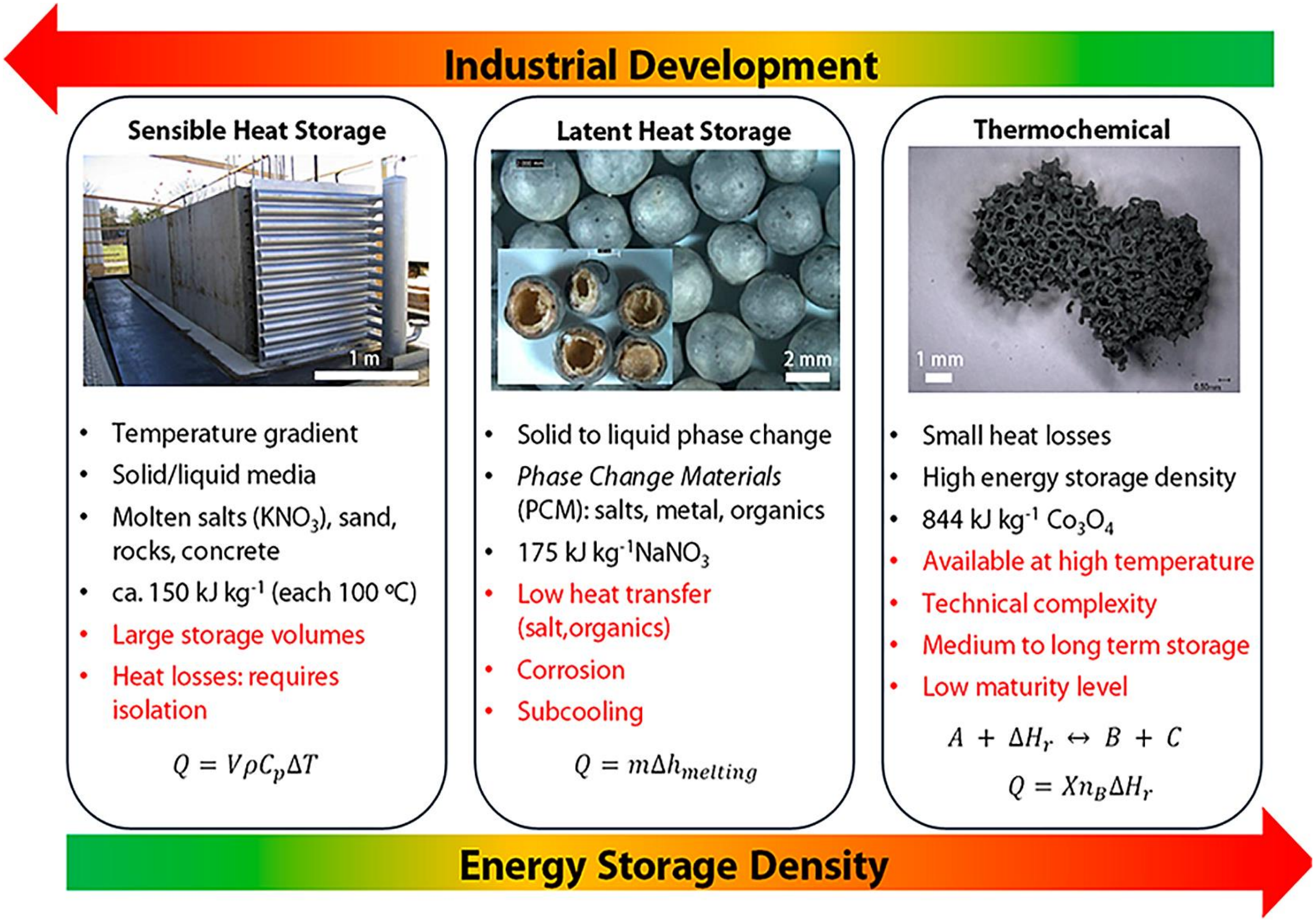
Energy storage



*Power-to-Gas technologies are a potential source of low-cost, long-duration energy storage. Research, development and demonstration of this group of technologies is ongoing, and cost and performance data is evolving as of the time of writing. Hydrogen is the most developed candidate but other chemistries such as ammonia and methane are being investigated.

https://doi.org/10.1016/j.renene.2022.06.015

Thermal Energy Storage (TES)



Industrial Development

Sensible Heat Storage

- Temperature gradient
- Solid/liquid media
- Molten salts (KNO_3), sand, rocks, concrete
- ca. 150 kJ kg^{-1} (each 100 °C)
- Large storage volumes
- Heat losses: requires isolation

$$Q = V\rho C_p \Delta T$$

Latent Heat Storage

- Solid to liquid phase change
- *Phase Change Materials* (PCM): salts, metal, organics
- 175 kJ kg^{-1} $NaNO_3$
- Low heat transfer (salt,organics)
- Corrosion
- Subcooling

$$Q = m\Delta h_{melting}$$

Thermochemical

- Small heat losses
- High energy storage density
- 844 kJ kg^{-1} Co_3O_4
- Available at high temperature
- Technical complexity
- Medium to long term storage
- Low maturity level

$$A + \Delta H_r \leftrightarrow B + C$$

$$Q = X n_B \Delta H_r$$

Energy Storage Density

https://doi.org/10.1021/acs.chemrev.8b00315

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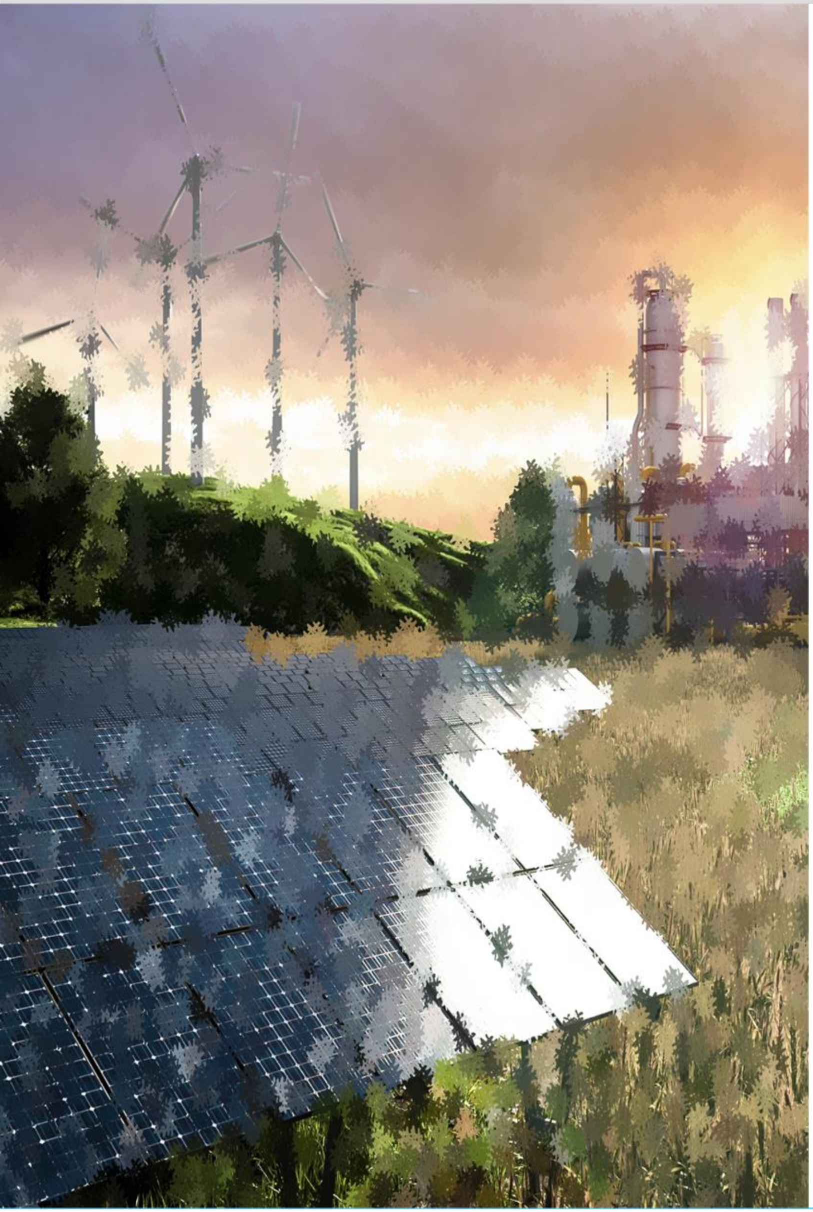
Outline

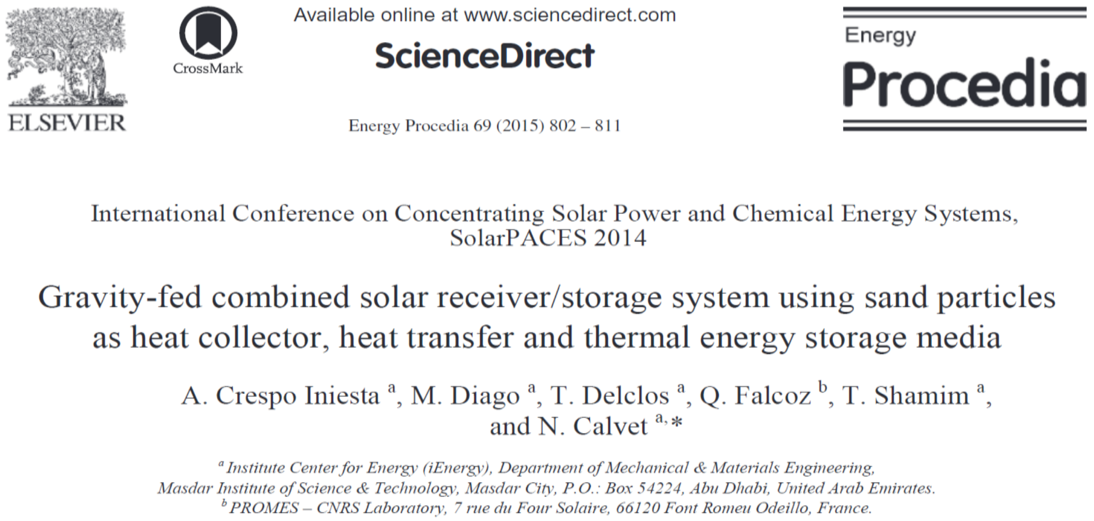


From sunlight and desert sand to a sustainable society

Thermochemical hydrogen storage: Redox reactor

Energy storage as metal ammine complexes

Sunlight and desert sand



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Energy
Procedia

International Conference on Concentrating Solar Power and Chemical Energy Systems,
SolarPACES 2014

Gravity-fed combined solar receiver/storage system using sand particles as heat collector, heat transfer and thermal energy storage media

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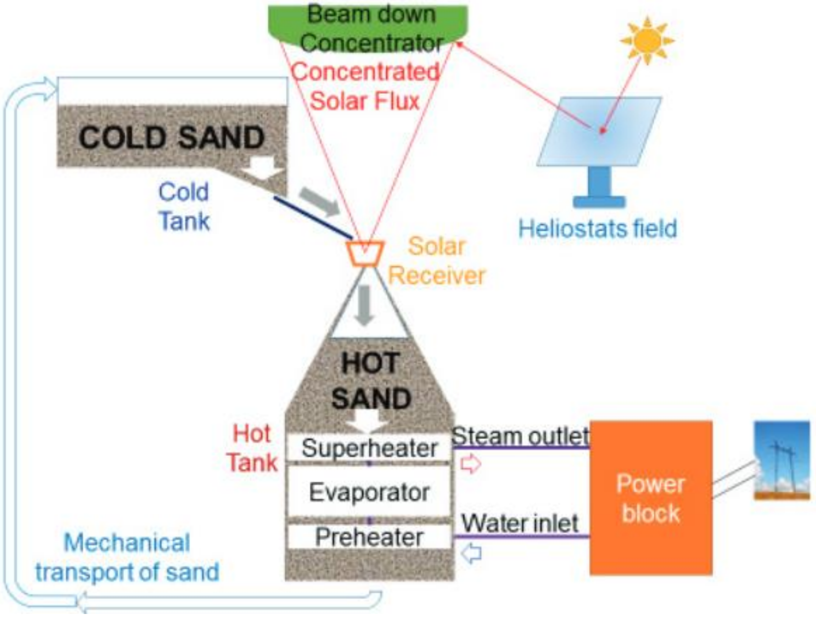

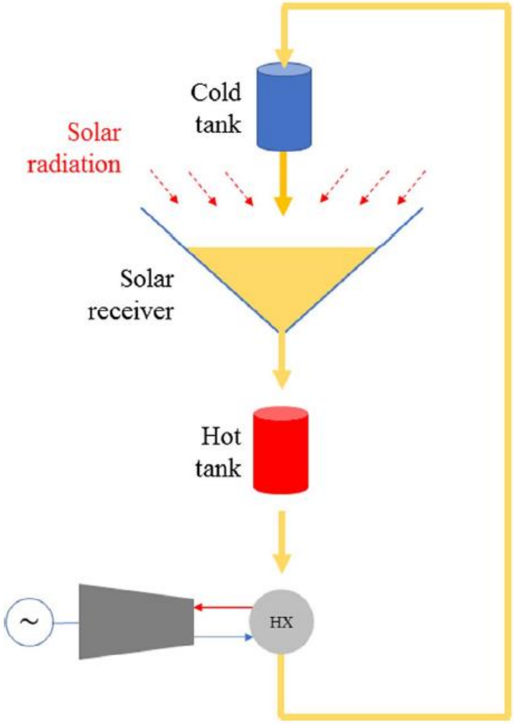

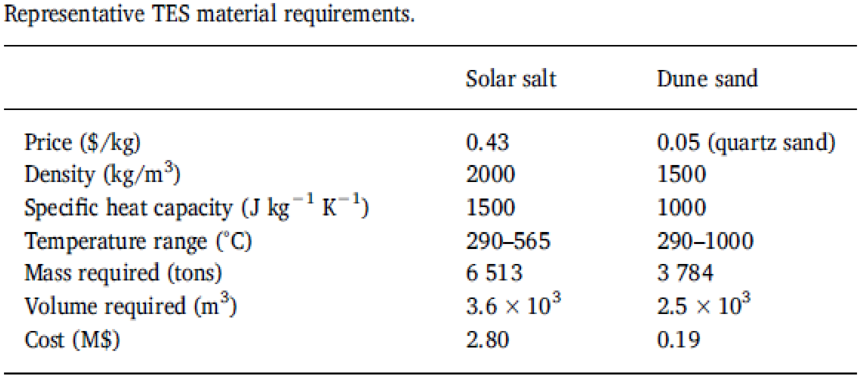

Representative TES material requirements.

	Solar salt	Dune sand
Price ($/kg)	0.43	0.05 (quartz sand)
Density (kg/m^3)	2000	1500
Specific heat capacity (J kg^{-1} K^{-1})	1500	1000
Temperature range (°C)	290–565	290–1000
Mass required (tons)	6 513	3 784
Volume required (m^3)	3.6×10^3	2.5×10^3
Cost (M$)	2.80	0.19

Why desert sand?

- Natural abundance of desert sand
- Costless local material
- Non corrosive and highly stable
- Sand stable up to 1000C

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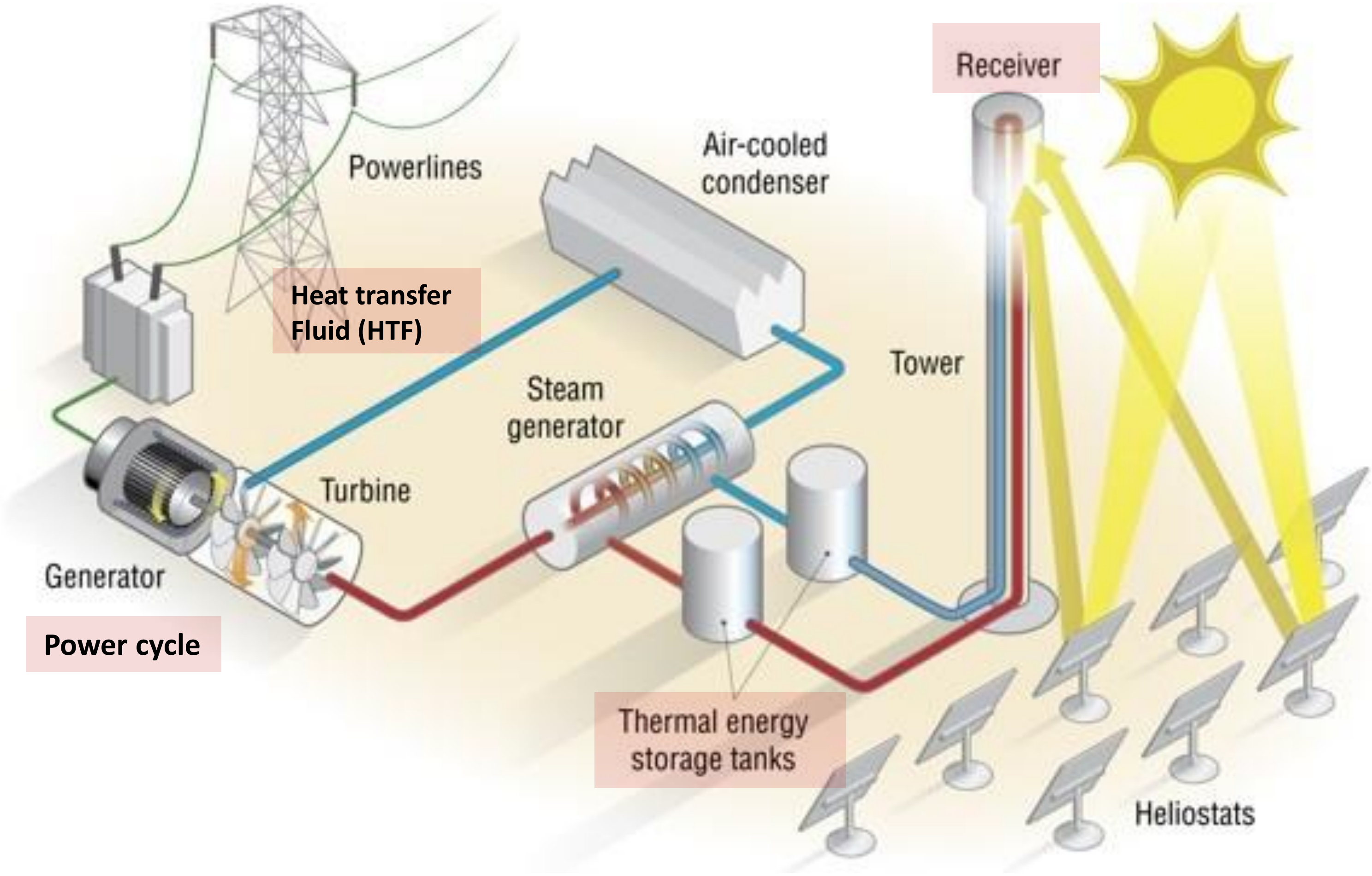
Components of CSP



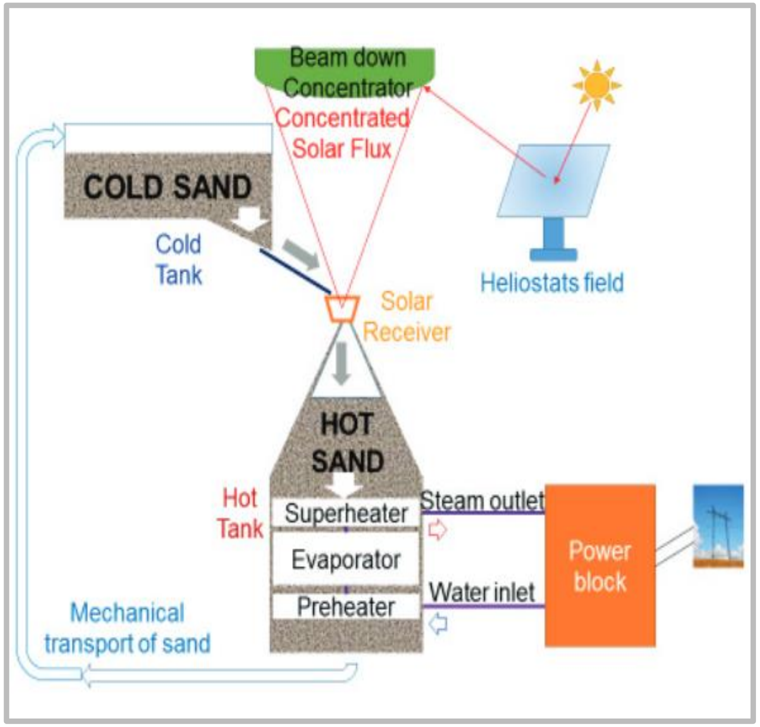
Desert sand

Near Sea
more
Calcium Carbonate

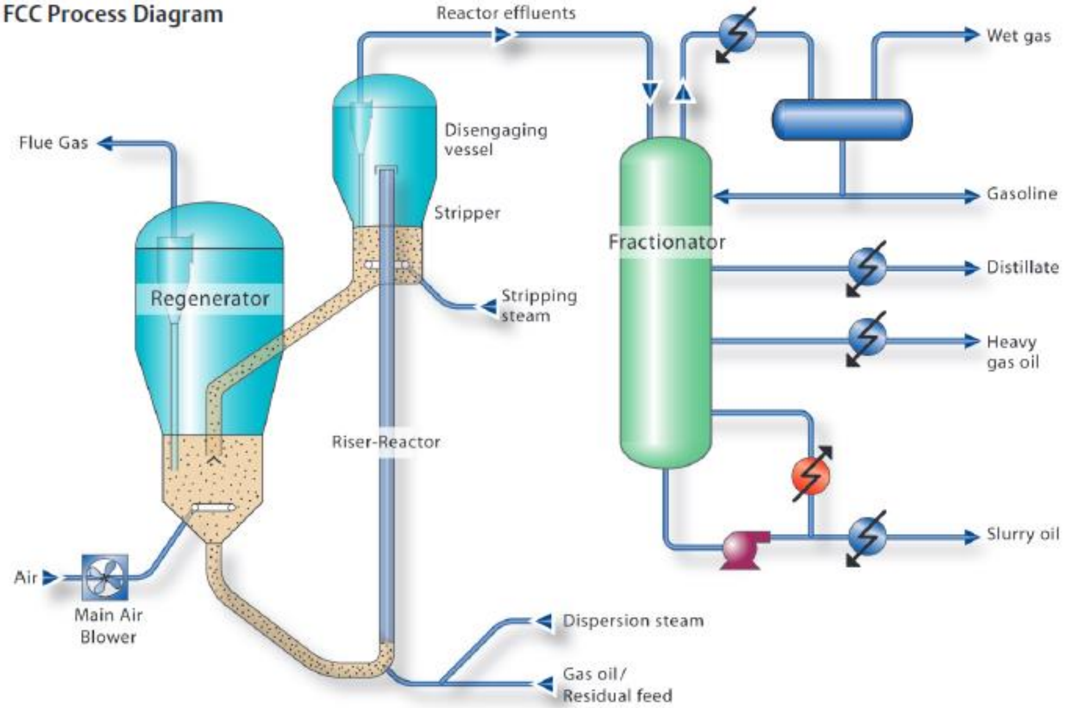
→

Further inland
more
Quartz

Conceptual design



Fluidized-bed Catalytic Cracker (FCC)



- Greater homogenisation
- Greater uniform outlet temperatures
- Higher heat transfer rates
- Increase in power production
- Increase in power cycle efficiency

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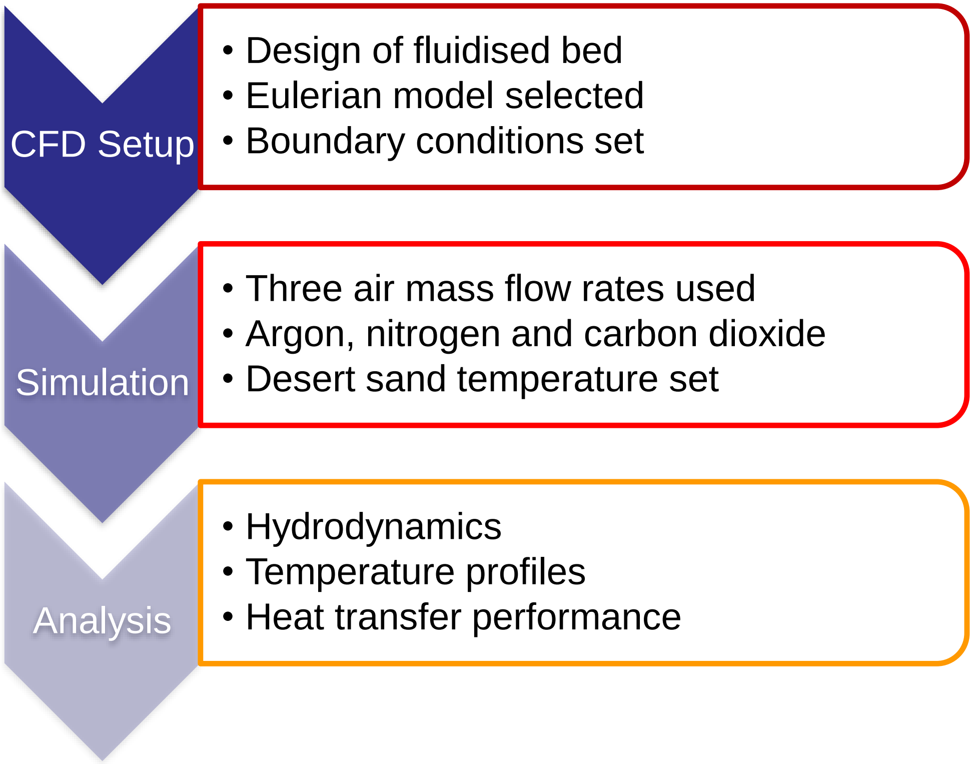
Solution approach

Computational fluid dynamics (**CFD**) was used to model a two-phase fluid flow in a fluidised bed system, where the desert sand constitutes the **TES** material and **HTF** the working fluid

The steps adopted to **optimize mass flow** and **heat transfer rate** were:



CFD Setup
- Design of fluidised bed
- Eulerian model selected
- Boundary conditions set

Simulation
- Three air mass flow rates used
- Argon, nitrogen and carbon dioxide
- Desert sand temperature set

Analysis
- Hydrodynamics
- Temperature profiles
- Heat transfer performance

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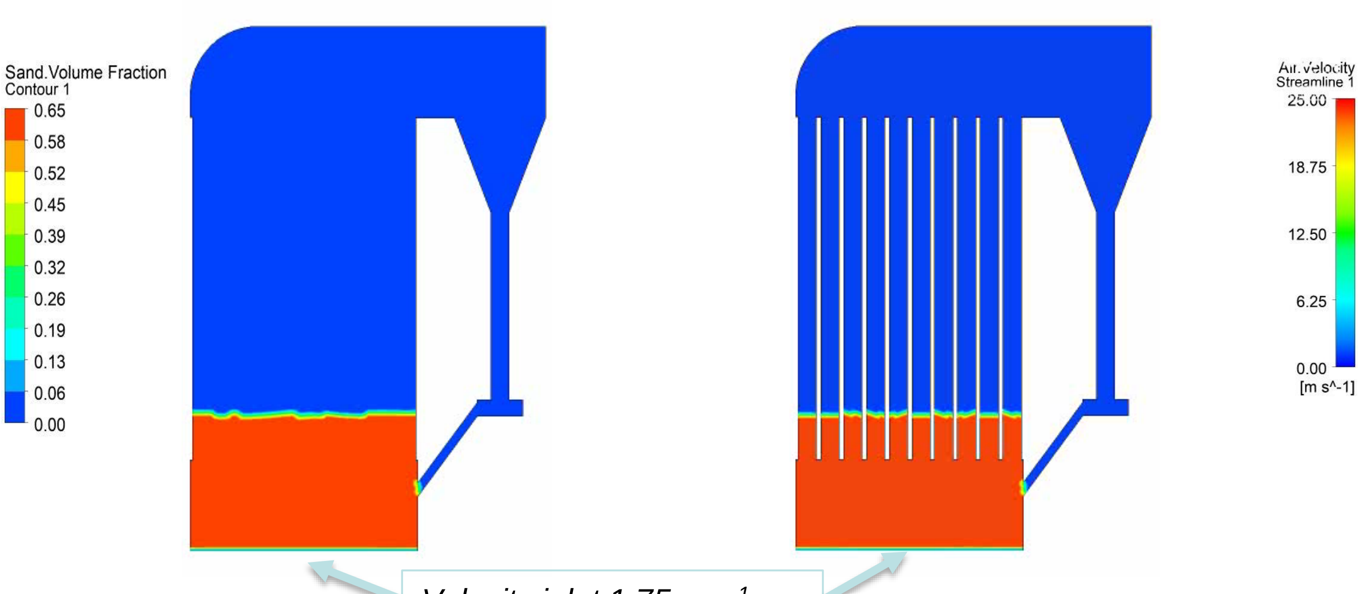
Circulating fluidised bed receiver design

- A circulating fluidised bed as the **heat exchanger,** TES material (desert sand) and the HTF (air)
- A **solar receiver** to reheat the sand

This design incorporate a solution to **minimise the pumping pressure costs** of the increased velocity required to circulate the sand.



Velocity inlet 1.75 m·s^{-1}

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Selection of Heat Transfer Fluid

Material	Density (kg·m^{-3})	Sp. Heat (J·kg^{-1}·K^{-1})	Thermal Cond. (W·m^{-1}·K^{-1})
Desert Sand	2650	755	0.242

- ***Air** was used as the initial HTF*
- **Three velocity** values of Air were initially analysed, 1.5, 1.75, and 2 m·s^{-1} to obtain the **optimum mass flow rate**

- The gases below were introduced in the simulation to analyse their **heat transfer characteristics** and to identify the optimum HTF.

Gas	Density (kg·m^{-3})	Velocity (m·s^{-1})	Specific Heat (J·kg^{-1}·K^{-1})	Mass flow rate (kg·s^{-1})
Air	1.23	1.75	1.006	1.071
Argon	1.62	1.32	0.526	1.071
Nitrogen	1.14	1.88	1.041	1.071
Carbon Dioxide	1.79	1.20	0.840	1.071

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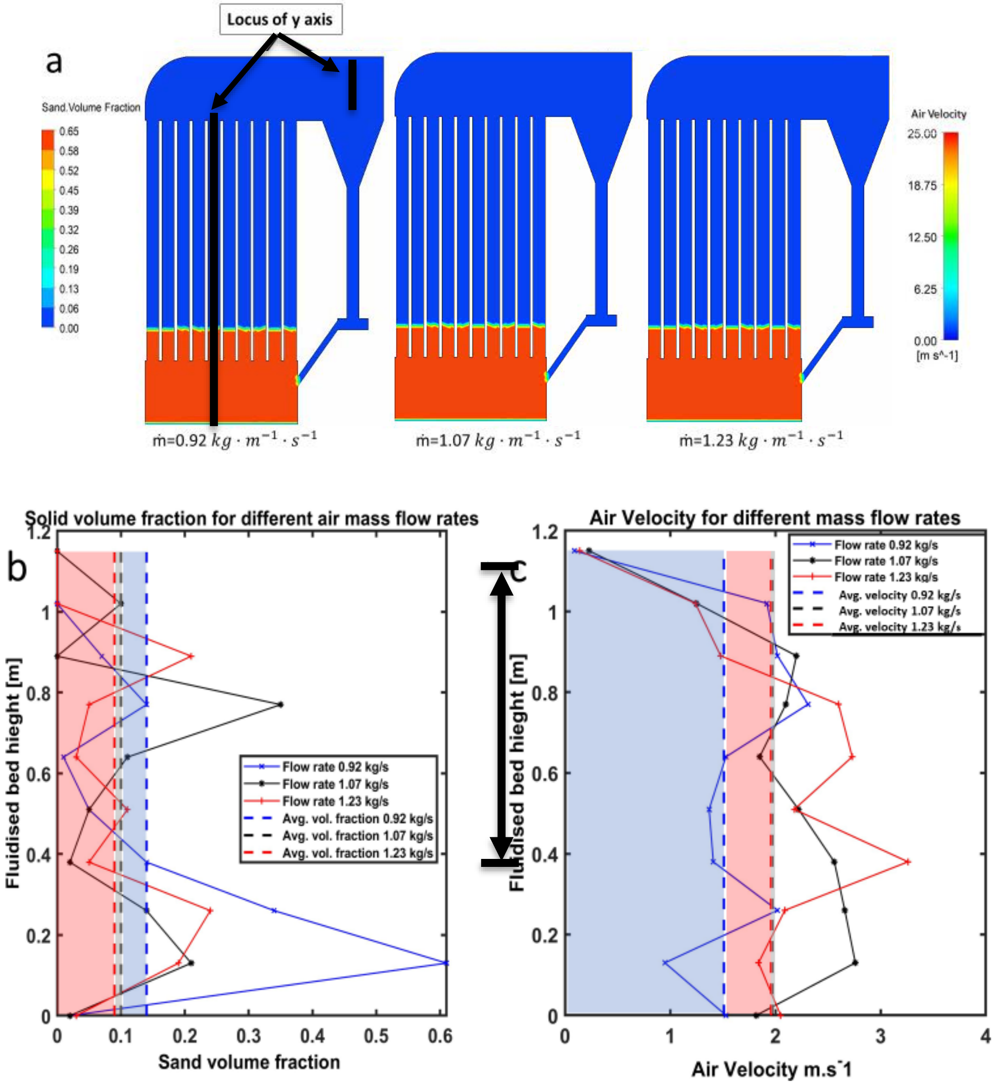
Optimizing mass flow rate

The gas mass flow rate passing through the bed was **modified to observe its effect on the fluidisation process, and to optimise the heat capacity of the gas** at outlet conditions.

The three superficial gas velocities used were v_g = 1.5, 1.75 and 2 m·s^{-1} corresponding to **air mass flow rates** of $\dot{m}_g$ **= 0.92, 1.07, and 1.23 kg·s^{-1}** respectively.

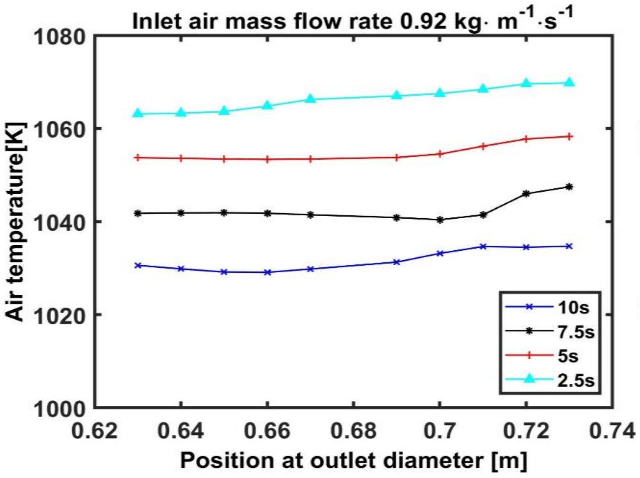
In terms of hydrodynamics, the **ideal range** of values for the mass flow rate lie between **1.07 and 1.23 kg·s^{-1}**

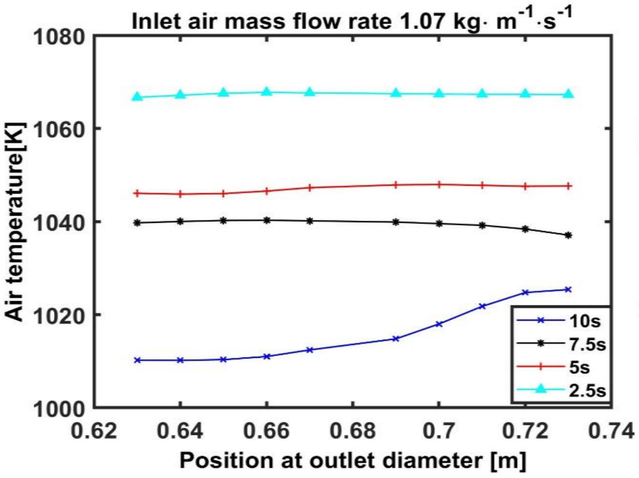
Pseudo-steady fluidisation conditions unfold at flow time t_{flow}=2 s.

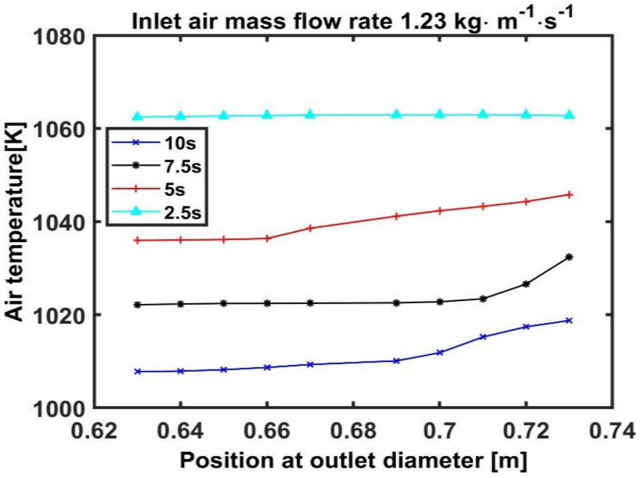


Different mass flowrates

- The effect of the mass flow rate on the transient evolution of the gas temperature at outlet conditions has been studied
- **All flowrates produce similar outlet temperatures**
- Although little difference between the three (≈2% with respect to the temperature change along the device), the greatest temperatures are observed at $\dot{m}_g$ = 0.92 kg·s^{-1}

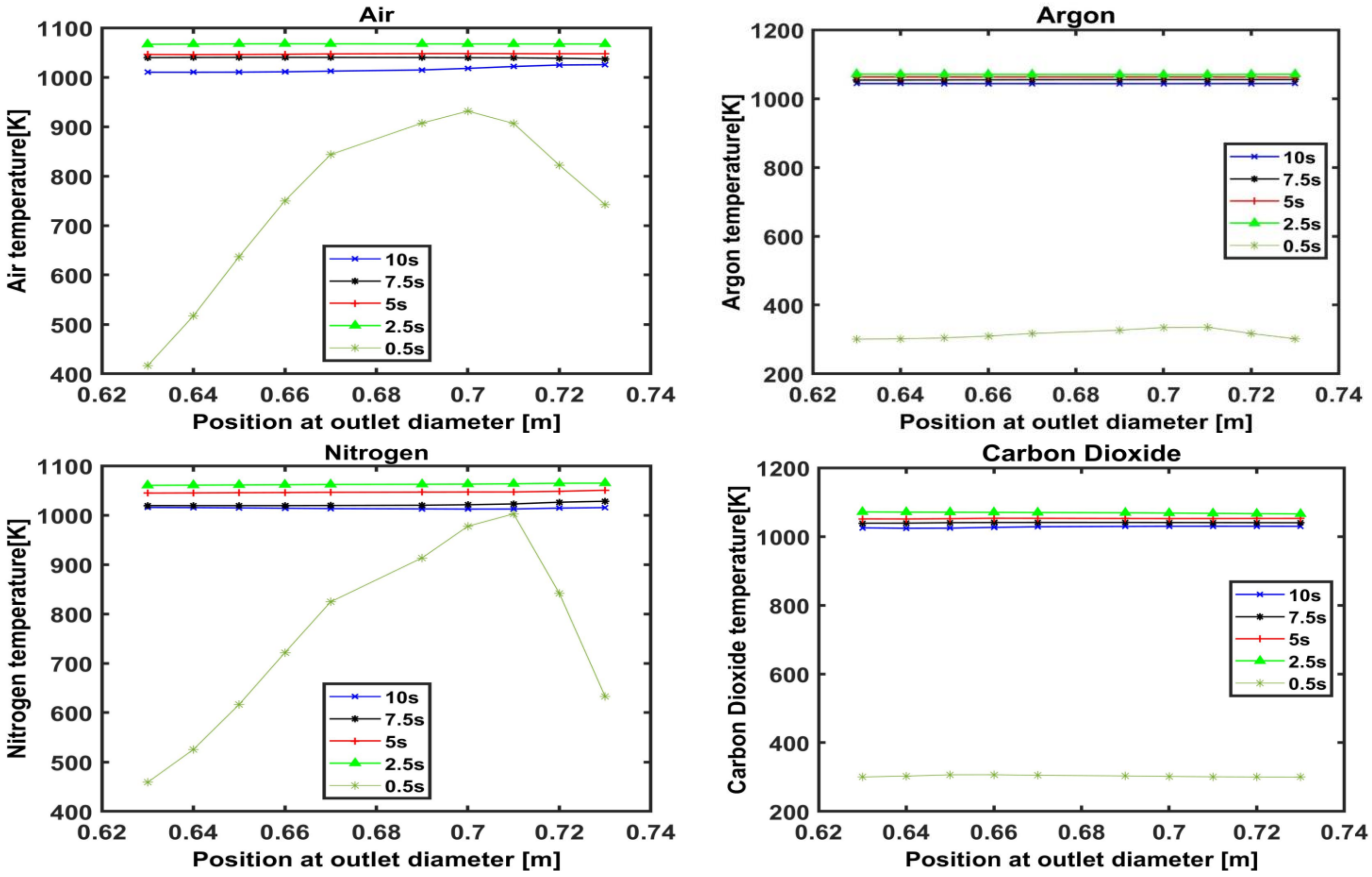






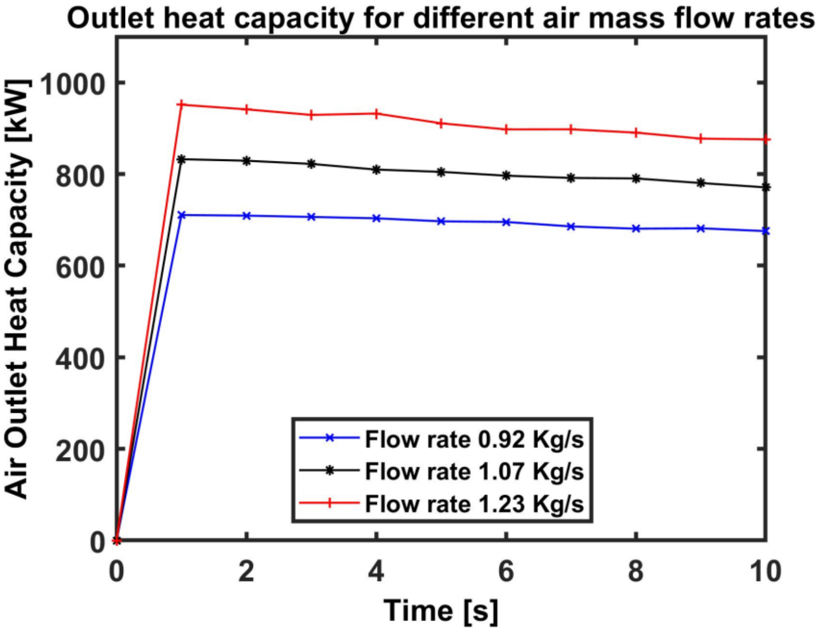
Different HTF – Air, Ar, N_2, CO_2

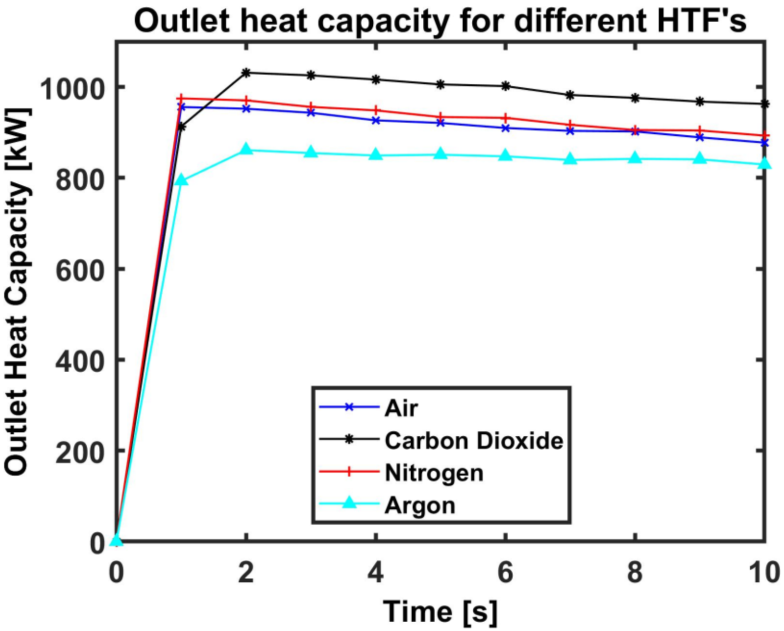
- **All HTF produce similar outlet temperatures**



Heat transfer comparison

Increasing the mass flow rate will slightly decrease the outlet temperature. However, **the slightly higher temperature of the lowest mass flow rate is not large enough to produce a higher power output**.

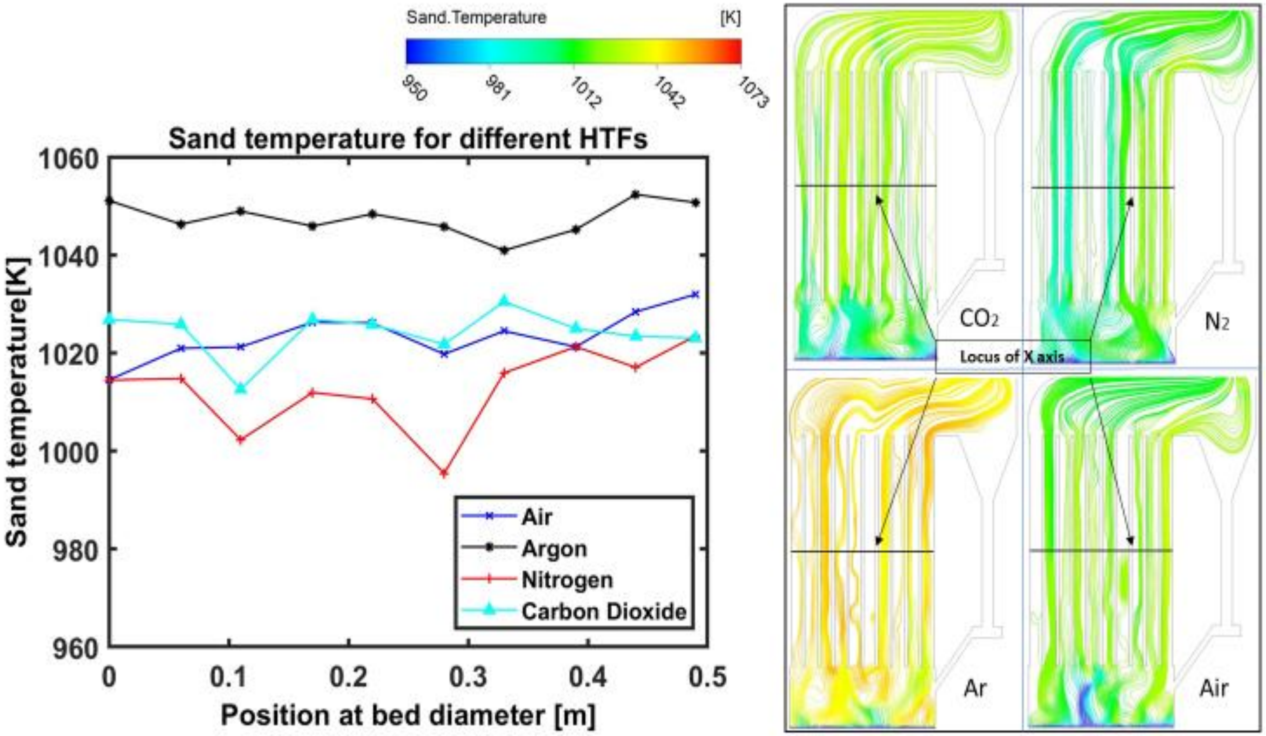




Sand temperature profiles

As shown the gas used as the HTF has a clear effect on the temperature attained by the solid phase:

Carbon dioxide produces a more stable solid phase temperature and a more uniform streamline



Cost analysis

Carbon dioxide has given the best results regarding stability and power output, but **is it feasible** option from the economic point of view

The results show that for a **mass flow rate of 1.07 kg·s^{-1}**

$$Net\ Profit\ [£ \cdot \boldsymbol{h}^{-1}] = Cost\ of\ Power\ Consumed - Profit\ of\ heat\ transferred\ to\ HTF$$

For carbon dioxide, the cost of circulating the gas represented 0.8% of the profit associated to the enthalpy change.

Gas	Power consumed [kW]	Power produced [kW]	Cost of power consumed [£·h^{-1}]	Profit of power produced [£·h^{-1}]	Net profit [£·h^{-1}]
Air	**17.96**	**955.83**	2.24	119.47	**117.23**
Ar	11.35	861.04	1.42	107.62	106.2
N_2	17.20	974.86	2.15	121.85	119.7
CO_2	**8.28**	**1031.32**	**1.03**	128.91	**127.88**

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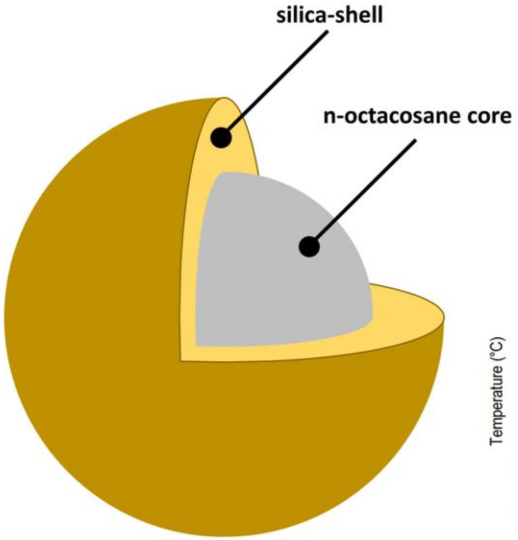
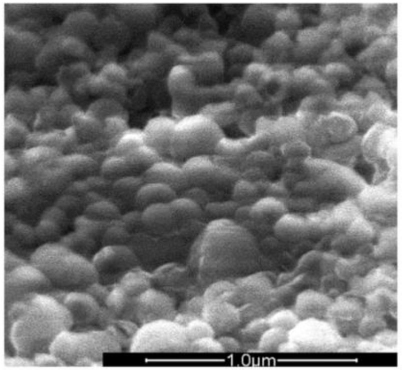
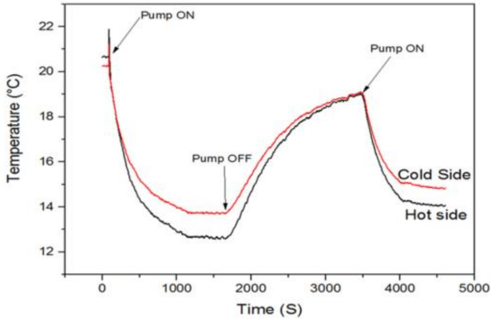
Synthesis and characterisation of *n-octacosane@silica*

To potentially stabilize the power output of the conceptual concentrated solar power design, an encapsulated material with silica shell and a melting n-octacosane core was proposed.







Material	Density (kg·m^{-3})	Sp. Heat (kJ·kg^{-1}·K^{-1})	Thermal Cond. (W·m^{-1}·K^{-1})
Desert Sand	2650	755	0.242
n-octacosane	807	1347	0.796

https://doi.org/10.1002/er.5039

The innovation:
Continuous circulating fluidised bed solar receiver dual heat exchanger

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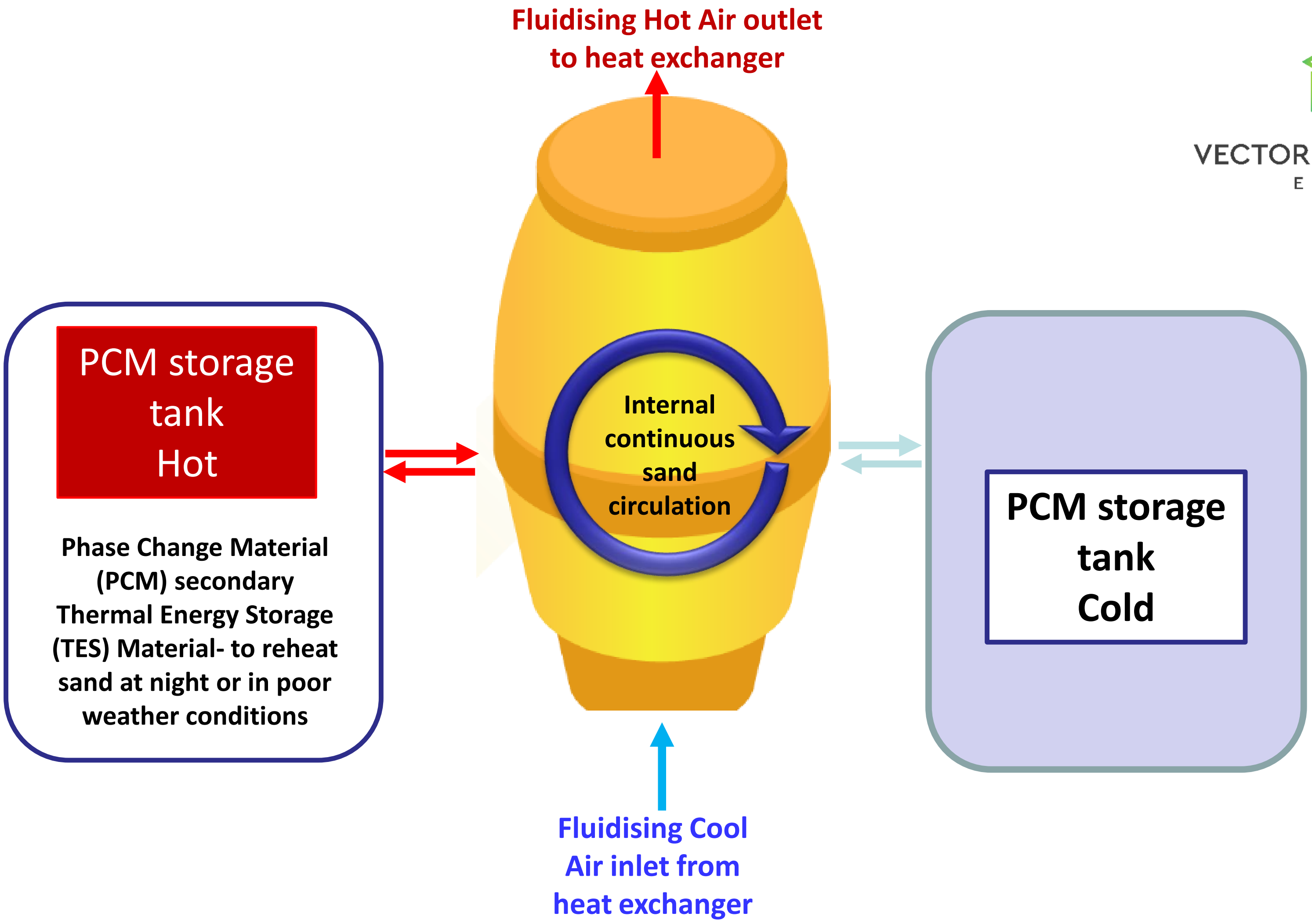
VECTOR SUSTAINABLE
ENERGY



Fluidising Hot Air outlet to heat exchanger

PCM storage tank
Hot

Phase Change Material (PCM) secondary Thermal Energy Storage (TES) Material- to reheat sand at night or in poor weather conditions

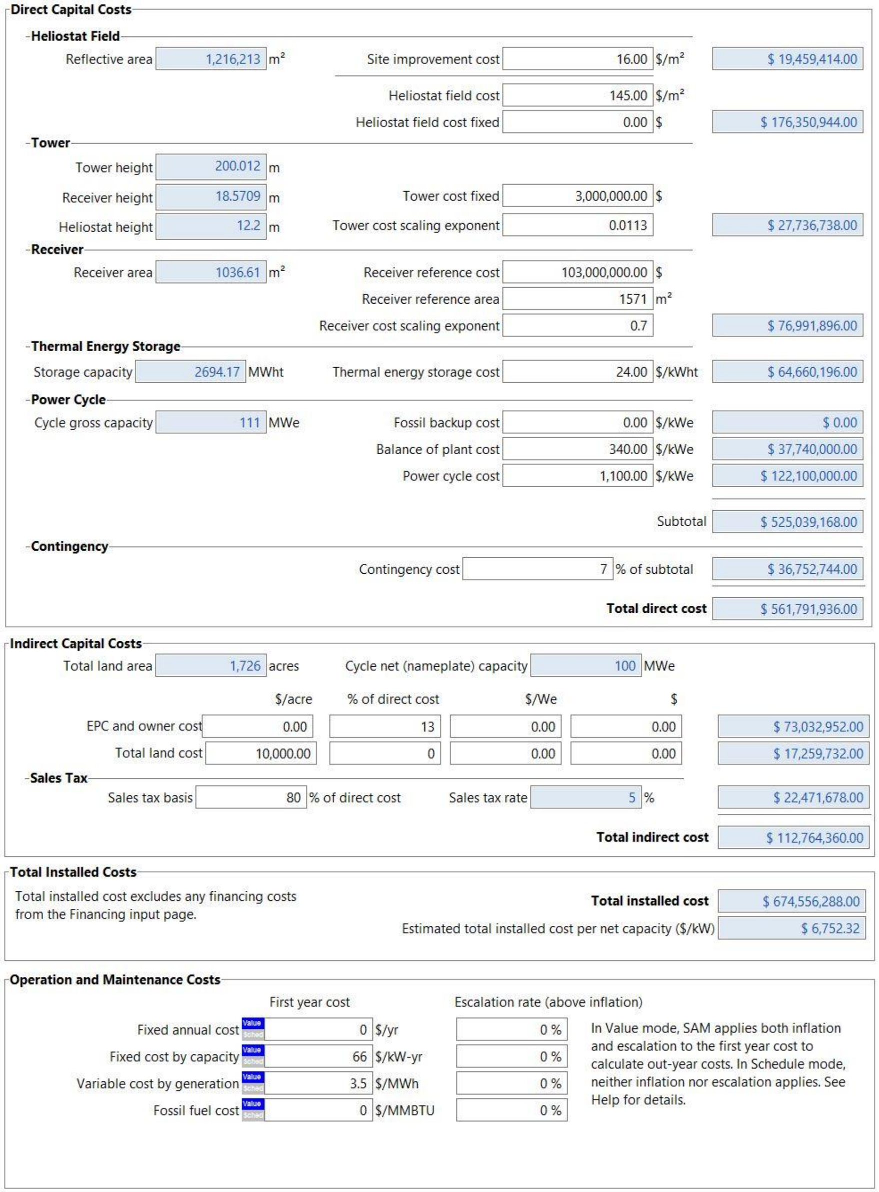
Internal continuous sand circulation

PCM storage tank Cold

Fluidising Cool Air inlet from heat exchanger

Restricted/ Prohibited use and/or distribution of this material

SAM cost break down



Direct Capital Costs

Heliostat Field

Reflective area	1,216,213	m²	Site improvement cost	16.00	$/m²	$ 19,459,414.00
			Heliostat field cost	145.00	$/m²	
			Heliostat field cost fixed	0.00	$	$ 176,350,944.00

Tower

Tower height	200.012	m				
Receiver height	18.5709	m	Tower cost fixed	3,000,000.00	$	
Heliostat height	12.2	m	Tower cost scaling exponent	0.0113		$ 27,736,738.00

Receiver

Receiver area	1036.61	m²	Receiver reference cost	103,000,000.00	$	
			Receiver reference area	1571	m²	
			Receiver cost scaling exponent	0.7		$ 76,991,896.00

Thermal Energy Storage

Storage capacity	2694.17	MWht	Thermal energy storage cost	24.00	$/kWht	$ 64,660,196.00

Power Cycle

Cycle gross capacity	111	MWe	Fossil backup cost	0.00	$/kWe	$ 0.00
			Balance of plant cost	340.00	$/kWe	$ 37,740,000.00
			Power cycle cost	1,100.00	$/kWe	$ 122,100,000.00
					Subtotal	$ 525,039,168.00

Contingency

Contingency cost	7	% of subtotal	$ 36,752,744.00
		Total direct cost	$ 561,791,936.00

Indirect Capital Costs

Total land area 1,726 acres Cycle net (nameplate) capacity 100 MWe

	$/acre	% of direct cost	$/We	$	
EPC and owner cost	0.00	13	0.00	0.00	$ 73,032,952.00
Total land cost	10,000.00	0	0.00	0.00	$ 17,259,732.00

Sales Tax

Sales tax basis 80 % of direct cost Sales tax rate 5 % $ 22,471,678.00

Total indirect cost $ 112,764,360.00

Total Installed Costs

Total installed cost excludes any financing costs from the Financing input page.

Total installed cost $ 674,556,288.00

Estimated total installed cost per net capacity ($/kW) $ 6,752.32

Operation and Maintenance Costs

	First year cost		Escalation rate (above inflation)
Fixed annual cost	0	$/yr	0 %
Fixed cost by capacity	66	$/kW-yr	0 %
Variable cost by generation	3.5	$/MWh	0 %
Fossil fuel cost	0	$/MMBTU	0 %

In Value mode, SAM applies both inflation and escalation to the first year cost to calculate out-year costs. In Schedule mode, neither inflation nor escalation applies. See Help for details.

System cost break down of a 100MW solar tower and how LCOE can be reduced using the novel design.

- **Reduced mirrors required**
- **Lower cost of tower height and receiver cost due to non corrosive sand and air.**
- **Desert sand is free compared to solar salt (24 $/kW).**
- **Land area cost reduction, less mirrors required.**
- **Lower operation and maintenance cost.**

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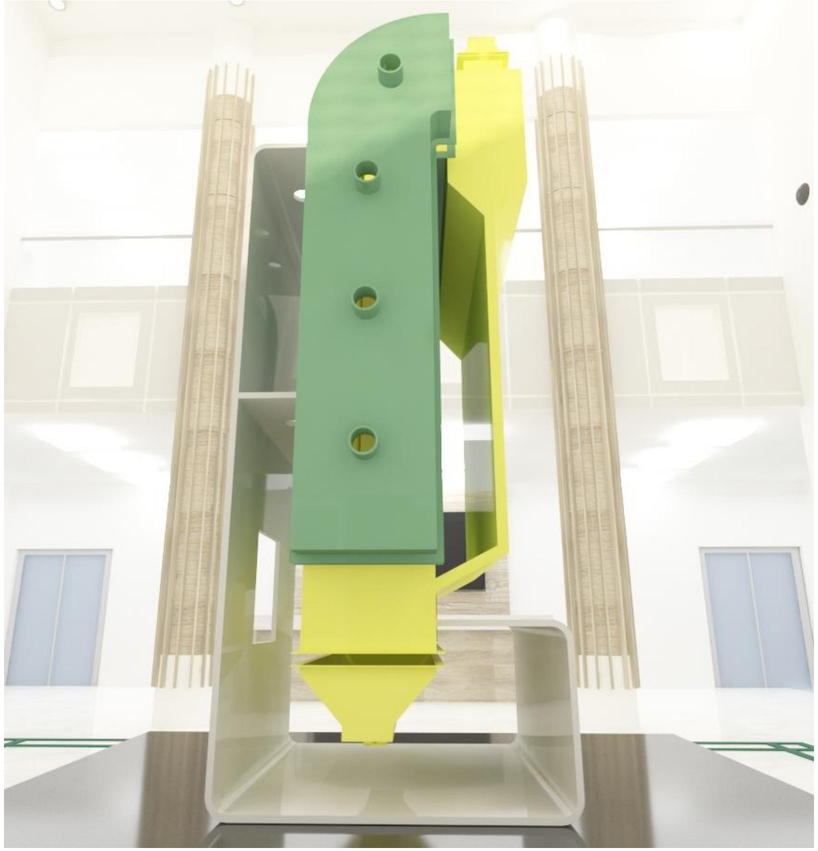
Vector Sustainable Energy Ltd - Start-up

VECTOR SUSTAINABLE
ENERGY



- **Vector Sustainable Energy Ltd** is a renewable energy startup looking to commercialise newly designed low cost sustainable concentrated solar power technology (CSP)
- This technology, a patented novel solar receiver design and process for CSP
- **It enables the continuous circulation and reheating of TES solid particles without mechanical aid. The use of nano/micro particle PCM as the secondary TES is also unique**

Restricted/ Prohibited use and/or distribution of this material

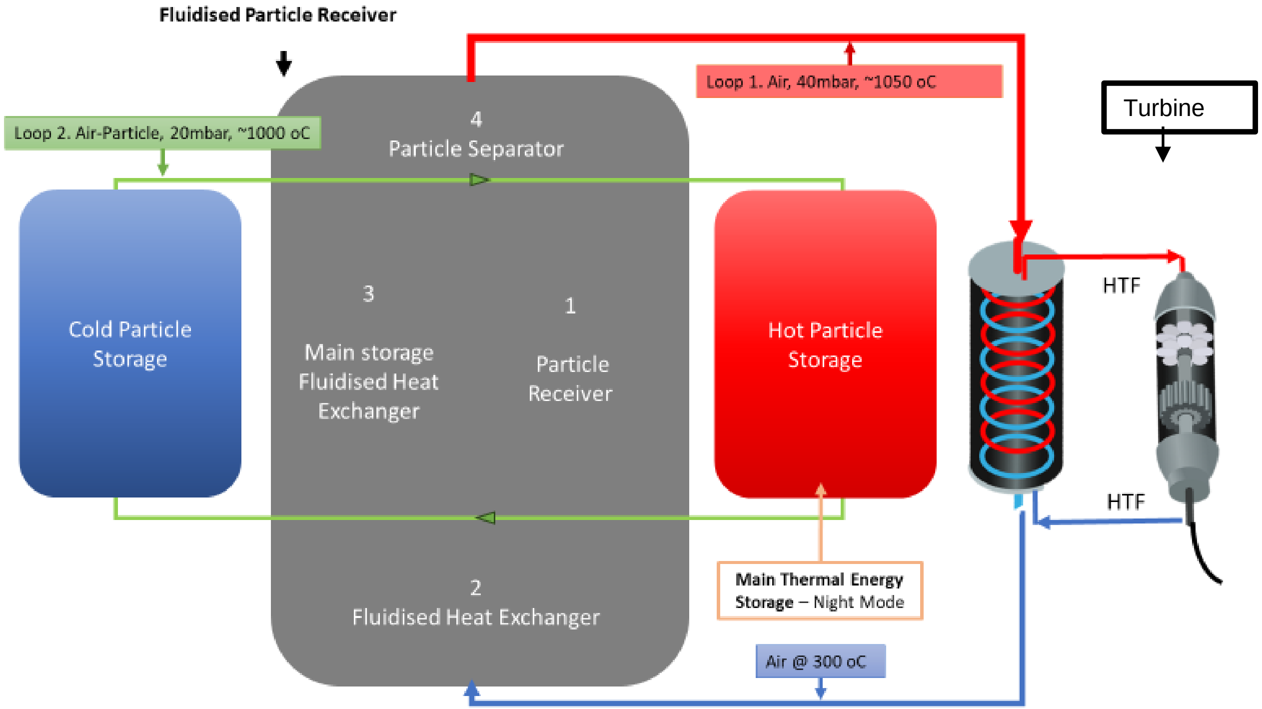
Our approach

- **Current TRL- 4 – working prototype**

IUK assessors score **9.4/10** InnovateUK grant awarded to develop successful next-gen CSP prototype

Advantages

- Aim for 24-hour Energy
- Greater power cycle efficiency
- >1000° C working temperature
- Micro Particles
- Three times the energy density
- Low-cost materials
- Multiple units
- Lower capital cost
- From 10kW to limit needed
- Device HEX efficiency ~99%
- Ultra-low pressure ~ 50 mbar
- Overall system efficiency >90%



Fluidised Particle Receiver

Loop 2. Air-Particle, 20mbar, ~1000 oC

Loop 1. Air, 40mbar, ~1050 oC

Turbine

Cold Particle Storage

4 Particle Separator

3 Main storage Fluidised Heat Exchanger

1 Particle Receiver

2 Fluidised Heat Exchanger

Hot Particle Storage

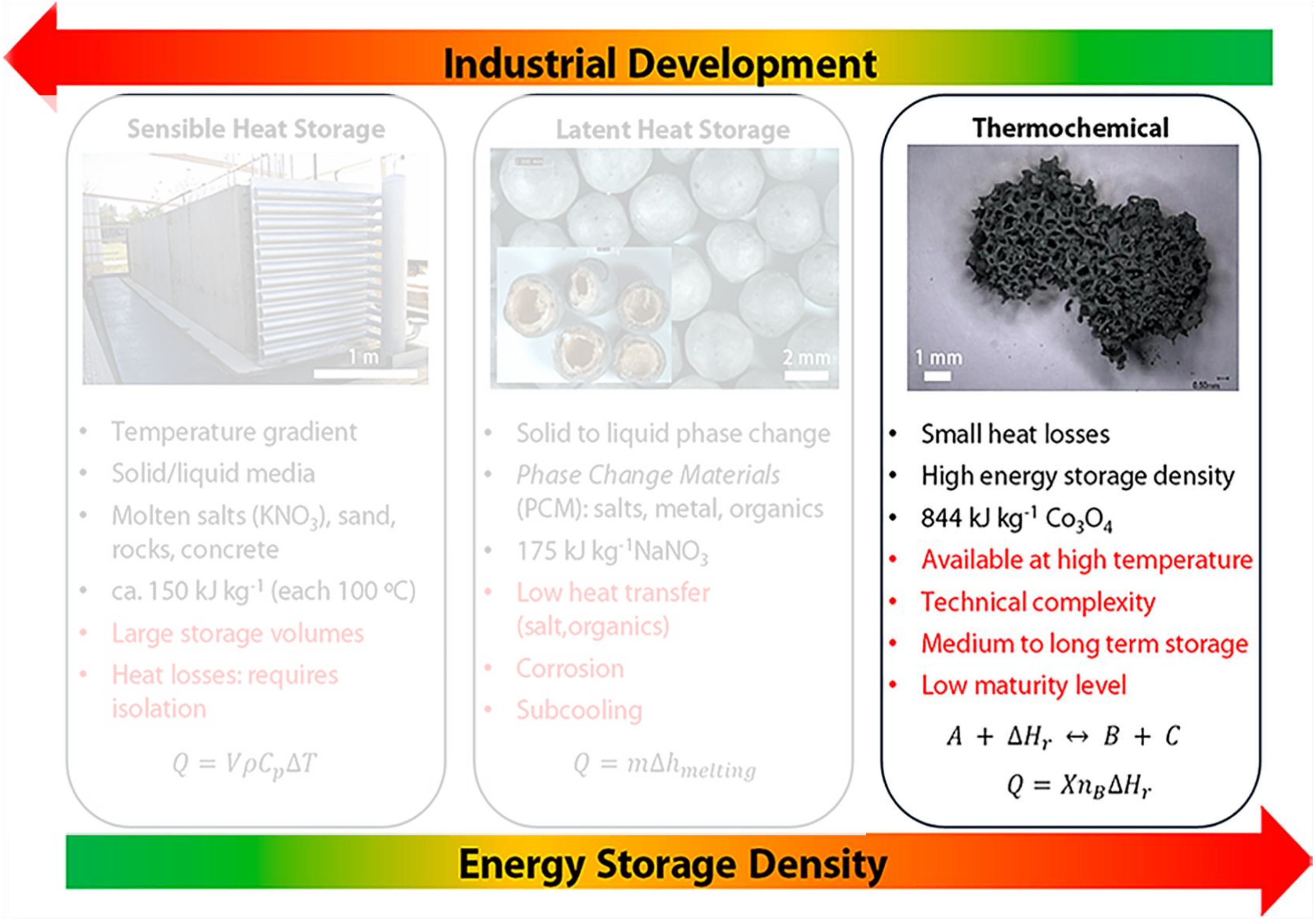
HTF

HTF

Main Thermal Energy Storage – Night Mode

Air @ 300 oC

Thermal energy storage (TES)



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- *Phase Change Materials* (PCM): salts, metal, organics
- 175 kJ kg^{-1} $NaNO_3$
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$$Q = m\Delta h_{melting}$$

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- Available at high temperature
- Technical complexity
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$$A + \Delta H_r \leftrightarrow B + C$$

$$Q = X n_B \Delta H_r$$

https://doi.org/10.1021/acs.chemrev.8b00315

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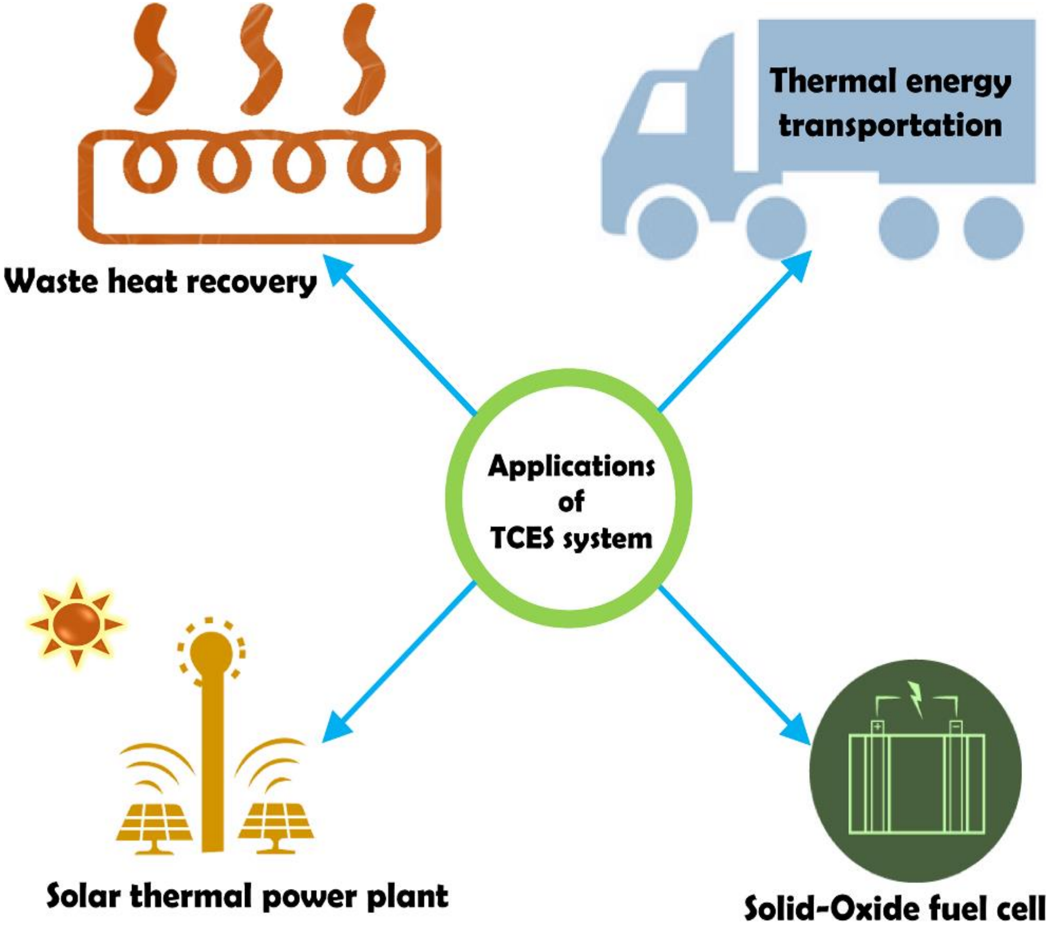
Thermochemical energy storage (TCES)

- High energy density
- High exergetic efficiency
- High operating temperature



https://doi.org/10.1016/j.apenergy.2019.113733

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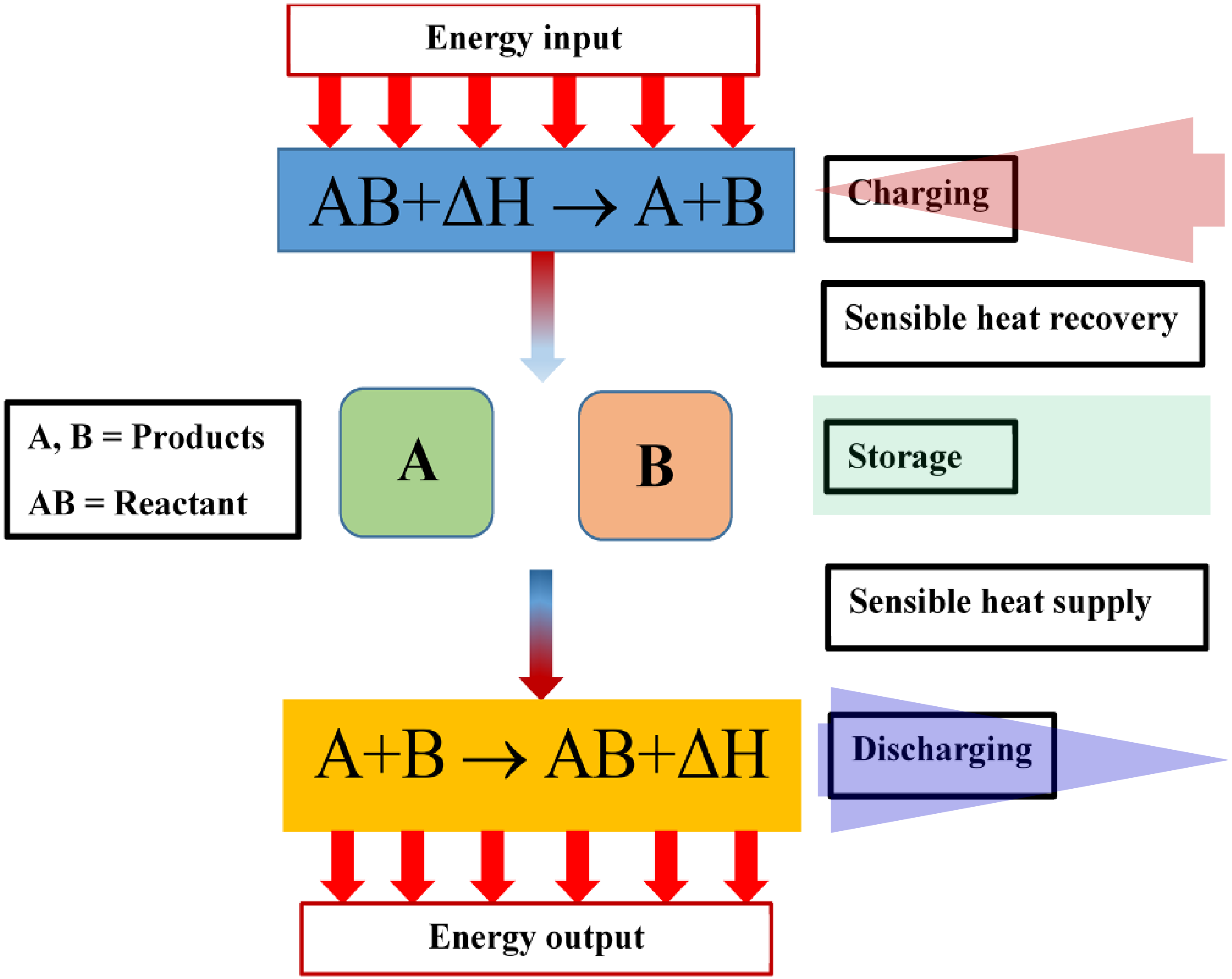
Thermochemical energy storage (TCES)



Energy input

$$AB + \Delta H \rightarrow A + B$$

Charging

Sensible heat recovery

A, B = Products

AB = Reactant

A

B

Storage

Sensible heat supply

$$A + B \rightarrow AB + \Delta H$$

Discharging

Energy output

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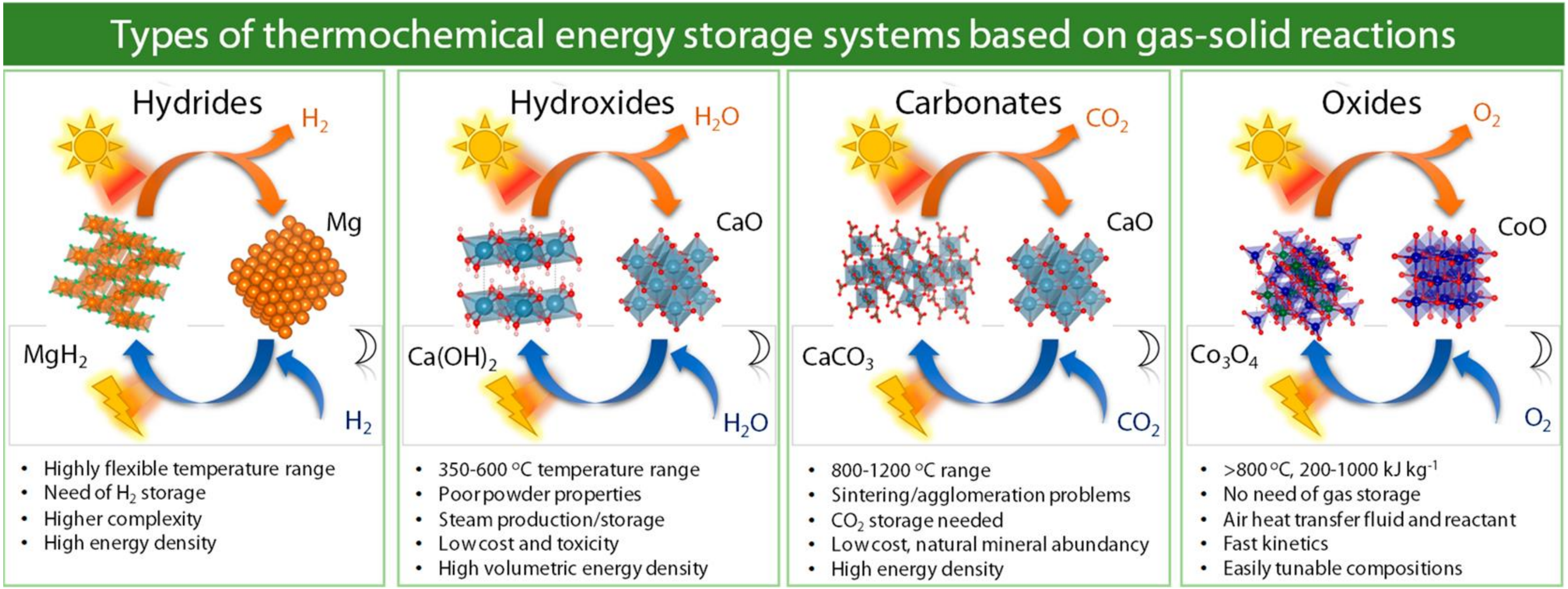
Thermochemical energy storage (TCES)



Hydrides

- Highly flexible temperature range
- Need of H_2 storage
- Higher complexity
- High energy density

Hydroxides

- 350-600 °C temperature range
- Poor powder properties
- Steam production/storage
- Low cost and toxicity
- High volumetric energy density

Carbonates

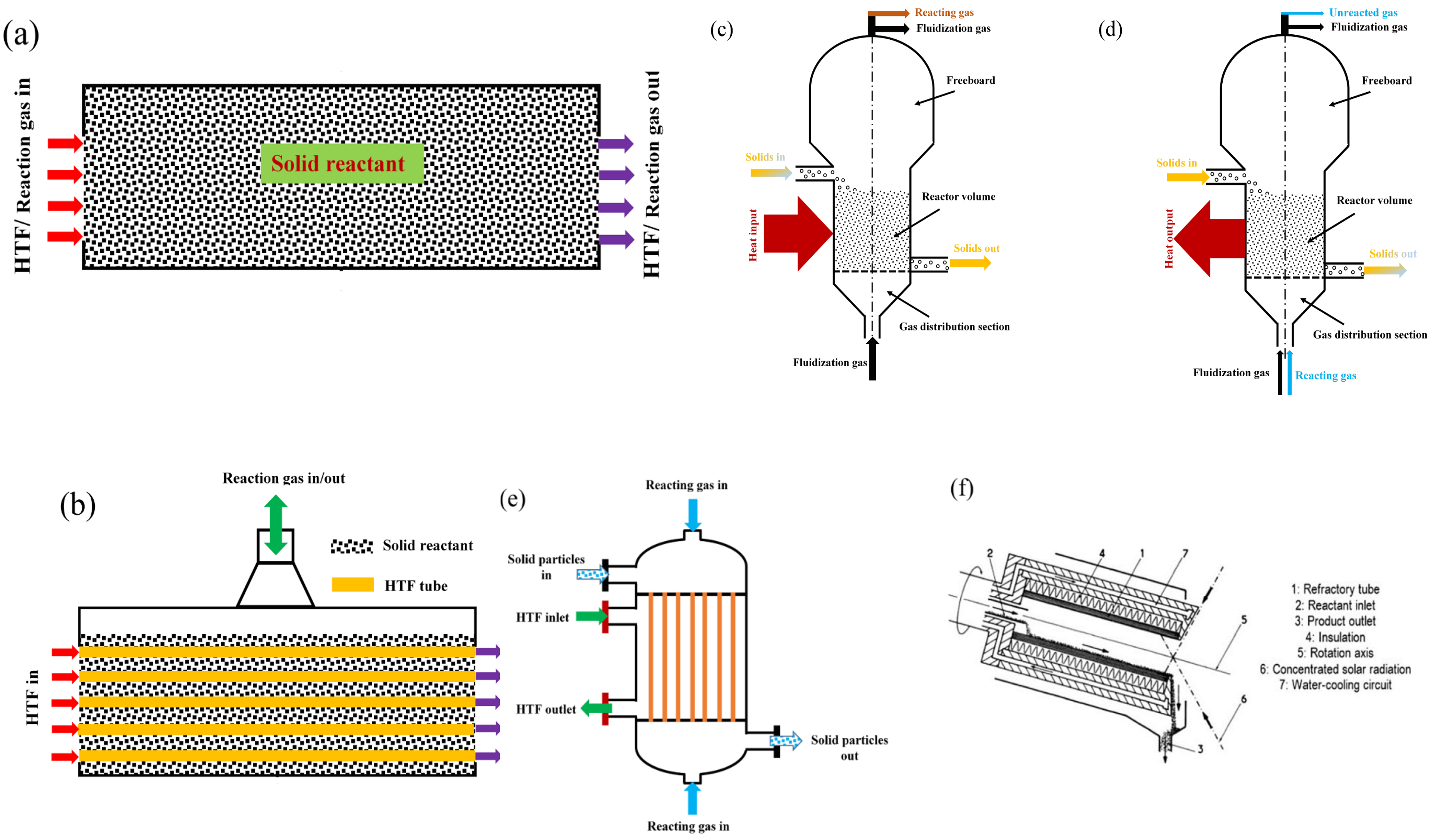
- 800-1200 °C range
- Sintering/agglomeration problems
- CO_2 storage needed
- Low cost, natural mineral abundancy
- High energy density

Oxides

- >800 °C, 200-1000 kJ kg^{-1}
- No need of gas storage
- Air heat transfer fluid and reactant
- Fast kinetics
- Easily tunable compositions

https://doi.org/10.1021/acs.chemrev.8b00315

Thermochemical energy storage (TCES)



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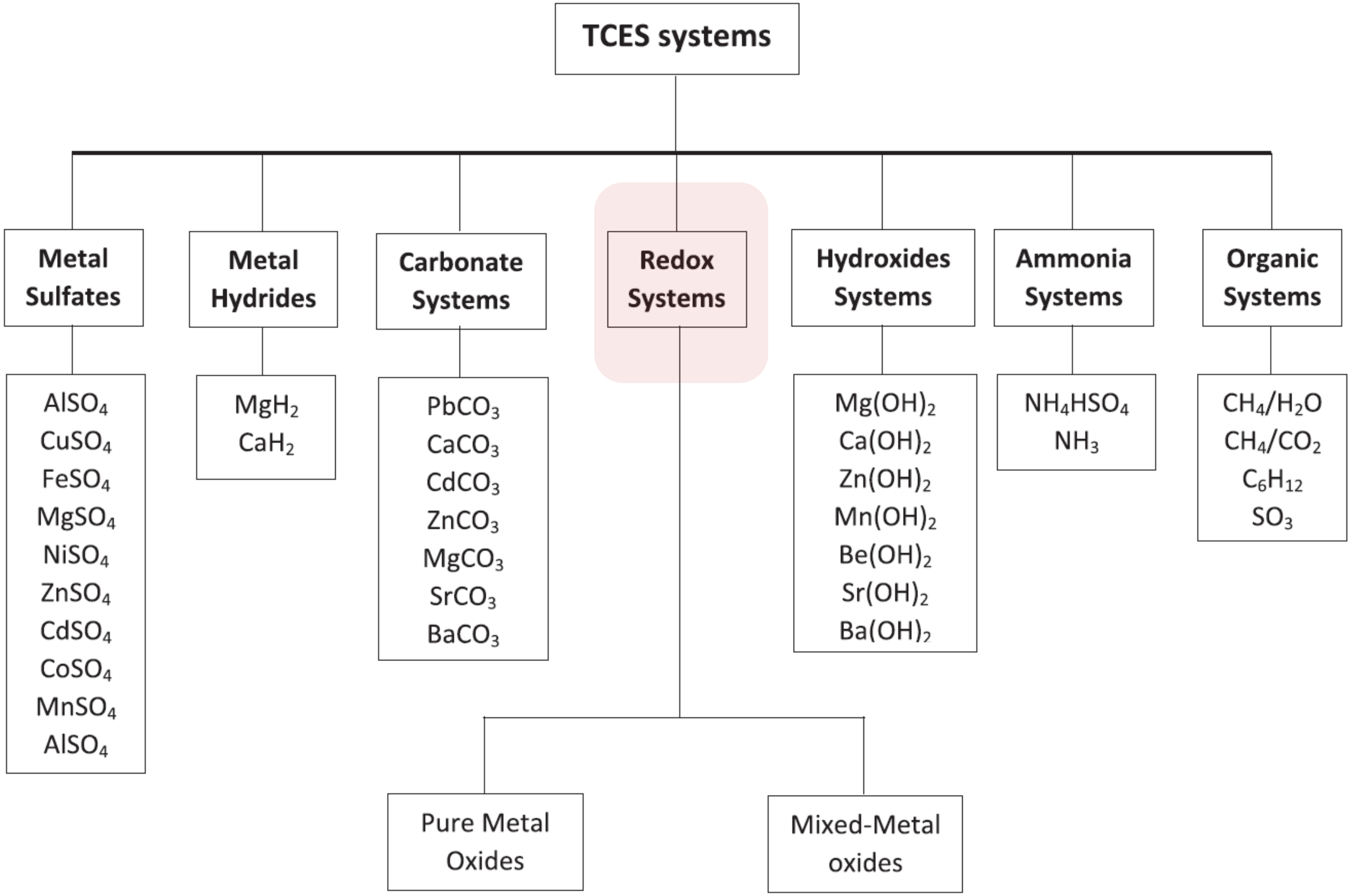
Thermochemical energy storage (TCES)

Thermochemical Hydrogen Storage



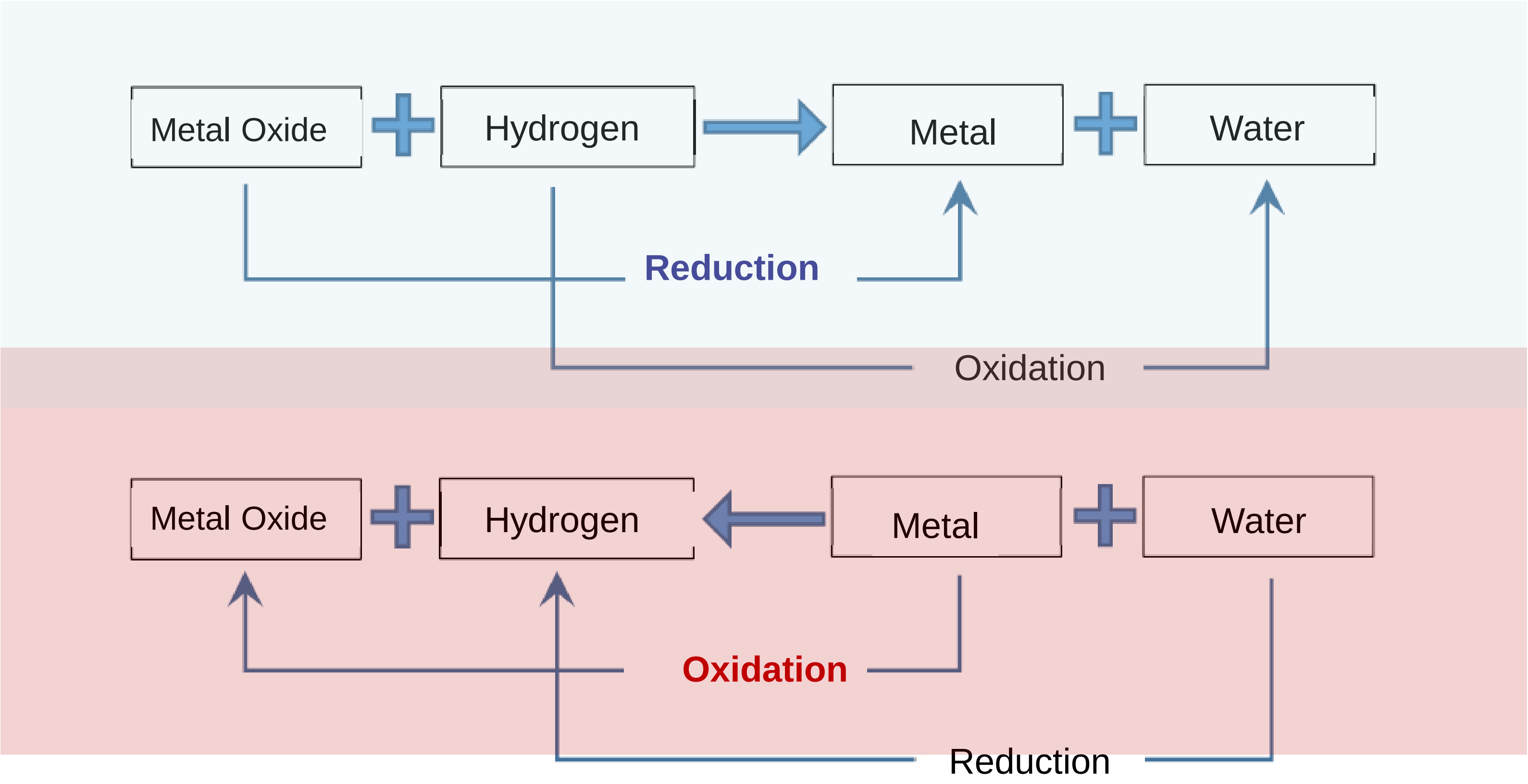
TCES systems

- **Metal Sulfates**
  - $AlSO_4$
  - $CuSO_4$
  - $FeSO_4$
  - $MgSO_4$
  - $NiSO_4$
  - $ZnSO_4$
  - $CdSO_4$
  - $CoSO_4$
  - $MnSO_4$
  - $AlSO_4$
- **Metal Hydrides**
  - MgH_2
  - CaH_2
- **Carbonate Systems**
  - $PbCO_3$
  - $CaCO_3$
  - $CdCO_3$
  - $ZnCO_3$
  - $MgCO_3$
  - $SrCO_3$
  - $BaCO_3$
- **Redox Systems**
  - Pure Metal Oxides
  - Mixed-Metal oxides
- **Hydroxides Systems**
  - $Mg(OH)_2$
  - $Ca(OH)_2$
  - $Zn(OH)_2$
  - $Mn(OH)_2$
  - $Be(OH)_2$
  - $Sr(OH)_2$
  - $Ba(OH)_2$
- **Ammonia Systems**
  - NH_4HSO_4
  - NH_3
- **Organic Systems**
  - CH_4/H_2O
  - CH_4/CO_2
  - C_6H_{12}
  - SO_3

https://doi.org/10.1016/j.rser.2018.09.004

Thermochemical Hydrogen Storage

$$\boxed{Me_xO_y + zH_2 \leftrightarrow Me_xO_{y-z} + zH_2O(g)}$$



Metal: **Ce, Cu, Fe, Mn, Ni, and W**

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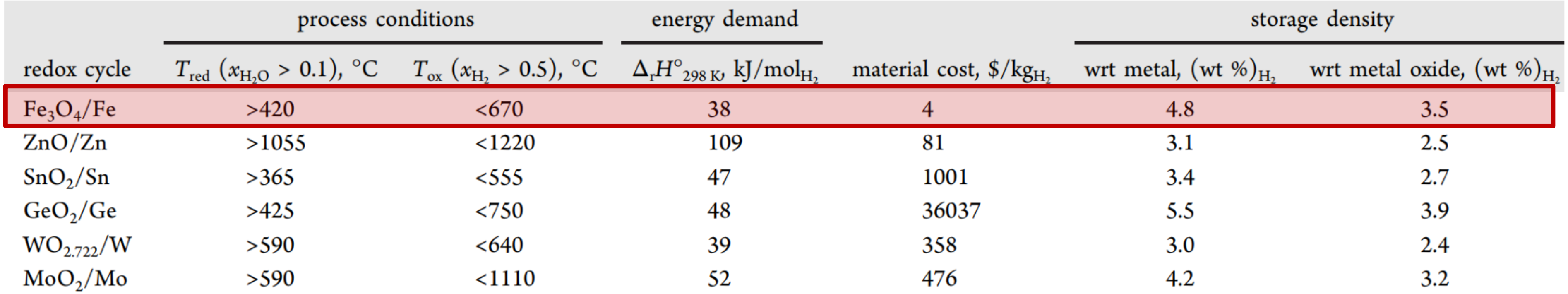
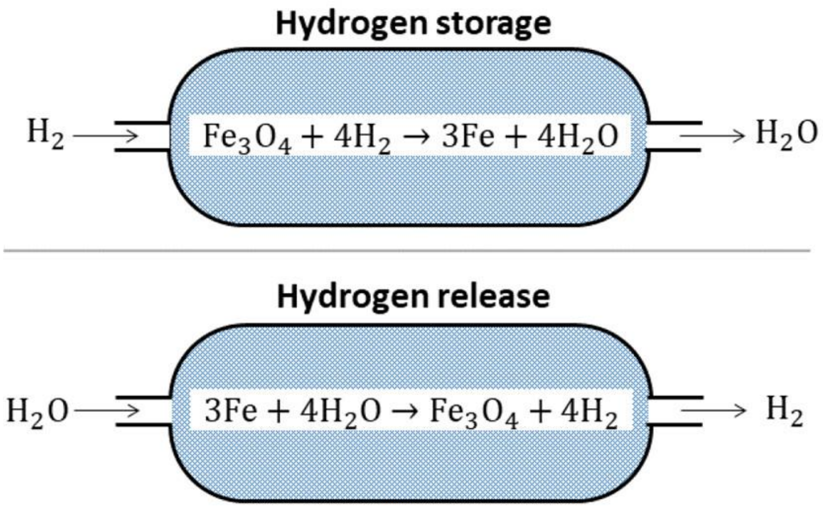
Thermochemical hydrogen storage: Redox reactions

$$Me_xO_y + zH_2 \leftrightarrow Me_xO_{y-z} + zH_2O(g)$$



	process conditions		energy demand		storage density	
redox cycle	T_{red} ($x_{H_2O} > 0.1$), °C	T_{ox} ($x_{H_2} > 0.5$), °C	$\Delta_r H°_{298\,K}$, kJ/mol$_{H_2}$	material cost, \$/kg$_{H_2}$	wrt metal, (wt %)$_{H_2}$	wrt metal oxide, (wt %)$_{H_2}$
Fe_3O_4/Fe	>420	<670	38	4	4.8	3.5
ZnO/Zn	>1055	<1220	109	81	3.1	2.5
SnO_2/Sn	>365	<555	47	1001	3.4	2.7
GeO_2/Ge	>425	<750	48	36037	5.5	3.9
$WO_{2.722}/W$	>590	<640	39	358	3.0	2.4
MoO_2/Mo	>590	<1110	52	476	4.2	3.2



https://doi.org/10.1021/acs.energyfuels.1c02615

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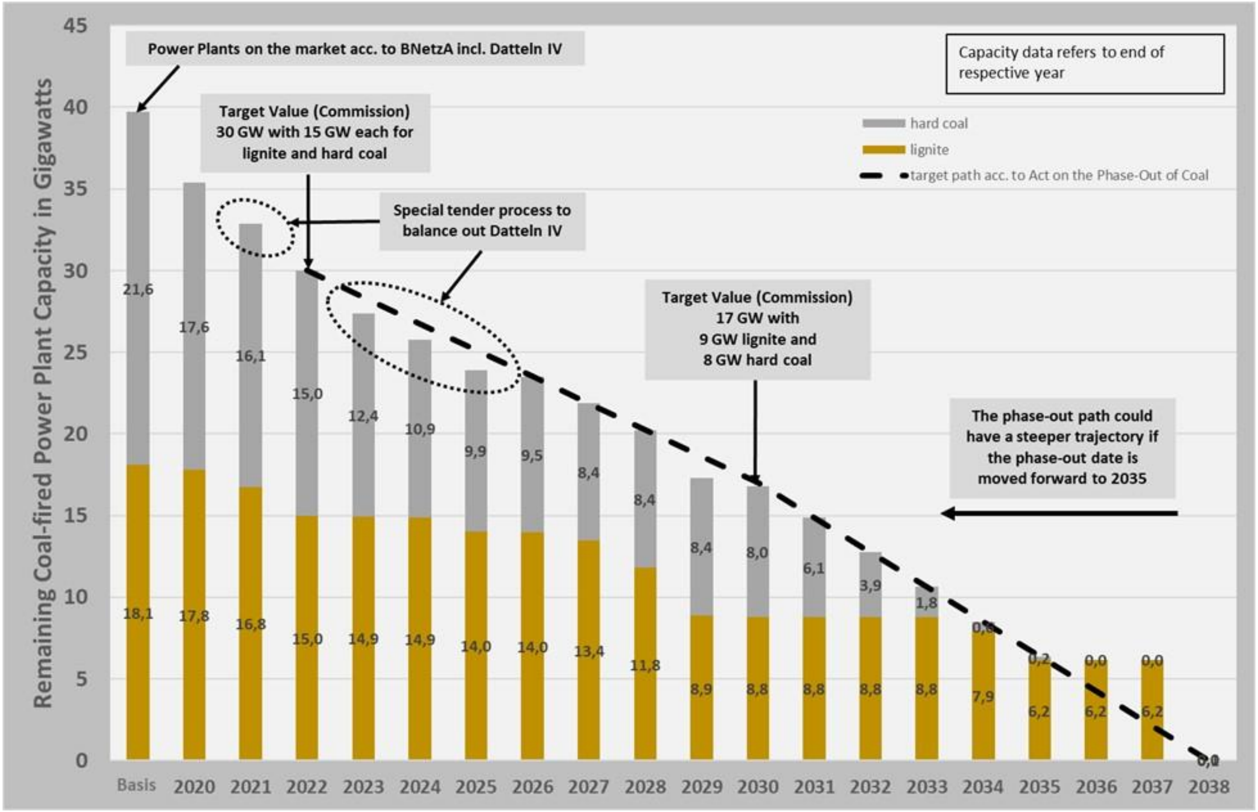
Phase-out of coal

- The Bundestag and Bundesrat adopted the gradual **phase-out of coal** power in July 2020

- Savings of more than **100 kilo tons CO_2** per day



Power Plants on the market acc. to BNetzA incl. Datteln IV

Capacity data refers to end of respective year

Target Value (Commission) 30 GW with 15 GW each for lignite and hard coal

Special tender process to balance out Datteln IV

Target Value (Commission) 17 GW with 9 GW lignite and 8 GW hard coal

The phase-out path could have a steeper trajectory if the phase-out date is moved forward to 2035

Agora Emergiewende. 2018. A future for Lusatia: A structural change plan for the Lusatia coal-mining region
https://www.bmuv.de/en/topics/climate-adaptation/climate-protection/national-climate-policy/translate-to-english-fragen-und-antworten-zum-kohleausstieg-in-deutschland

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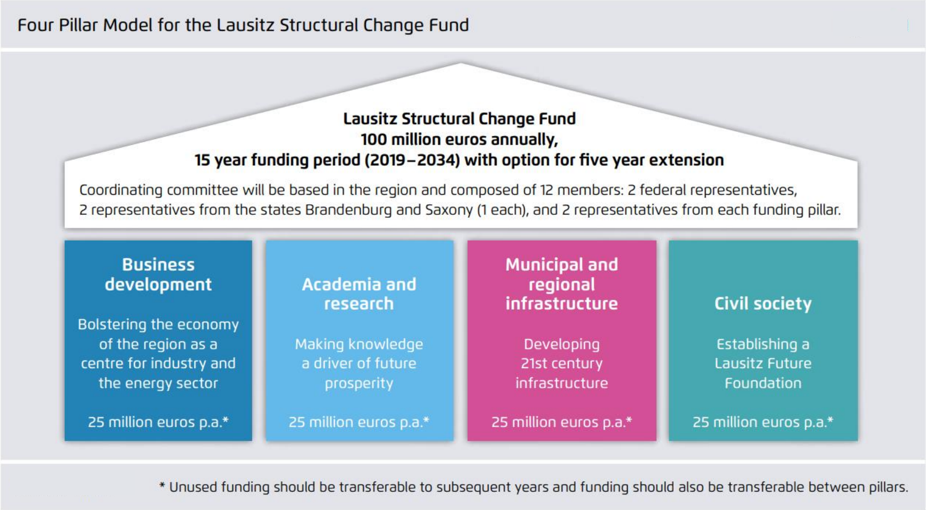
Structural change


© Elian Hadj-Hamdi


Four Pillar Model for the Lausitz Structural Change Fund

Lausitz Structural Change Fund
100 million euros annually,
15 year funding period (2019–2034) with option for five year extension

Coordinating committee will be based in the region and composed of 12 members: 2 federal representatives, 2 representatives from the states Brandenburg and Saxony (1 each), and 2 representatives from each funding pillar.

Business development	Academia and research	Municipal and regional infrastructure	Civil society
Bolstering the economy of the region as a centre for industry and the energy sector	Making knowledge a driver of future prosperity	Developing 21st century infrastructure	Establishing a Lausitz Future Foundation
25 million euros p.a.*	25 million euros p.a.*	25 million euros p.a.*	25 million euros p.a.*

* Unused funding should be transferable to subsequent years and funding should also be transferable between pillars.

- The German Federal Government and the Federal states support the **structural change** in the regions affected by the coal phase-out
- Up to €14 billion by 2038, 43% earmarked for **Lusatia**
- Over and above this, €26 billion to be invested in research and other assistance programs

Agora Energiewende. 2018. A future for Lusatia: A structural change plan for the Lusatia coal-mining region
https://www.bmuv.de/en/topics/climate-adaptation/climate-protection/national-climate-policy/translate-to-english-fragen-und-antworten-zum-kohleausstieg-in-deutschland

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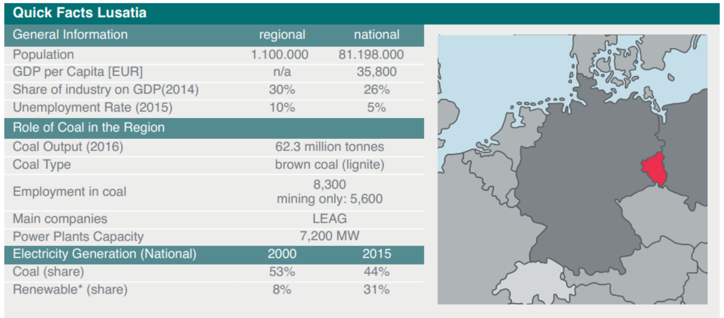
Cottbus

- ❑ Cottbus is the largest city and the economic center of the region of Lusatia
- ❑ **Lusatia** comprises a region in the eastern German states of Brandenburg and Saxony, and in south-western Poland
- ❑ Higher urban-rural divide
- ❑ Open-cast **lignite mining** area



Quick Facts Lusatia

General Information	regional	national
Population	1.100.000	81.198.000
GDP per Capita [EUR]	n/a	35,800
Share of industry on GDP(2014)	30%	26%
Unemployment Rate (2015)	10%	5%
Role of Coal in the Region		
Coal Output (2016)	62.3 million tonnes	
Coal Type	brown coal (lignite)	
Employment in coal	8,300 mining only: 5,600	
Main companies	LEAG	
Power Plants Capacity	7,200 MW	
Electricity Generation (National)	**2000**	**2015**
Coal (share)	53%	44%
Renewable* (share)	8%	31%

Spreng, E. 2011. Walking the line: Bilingual sorbs, emotions, and endangerment in Eastern Germany. PhD Thesis, University of Illinois
https://epub.wupperinst.org/frontdoor/deliver/index/docId/7167/file/7167_Phasing_Out_Coal.pdf
https://ieefa.org/wp-content/uploads/2016/09/A-Foundation-Based-Framework-for-Phasing-Out-German-Lignite-in-Lausitz_September2016.pdf

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Lignite mining

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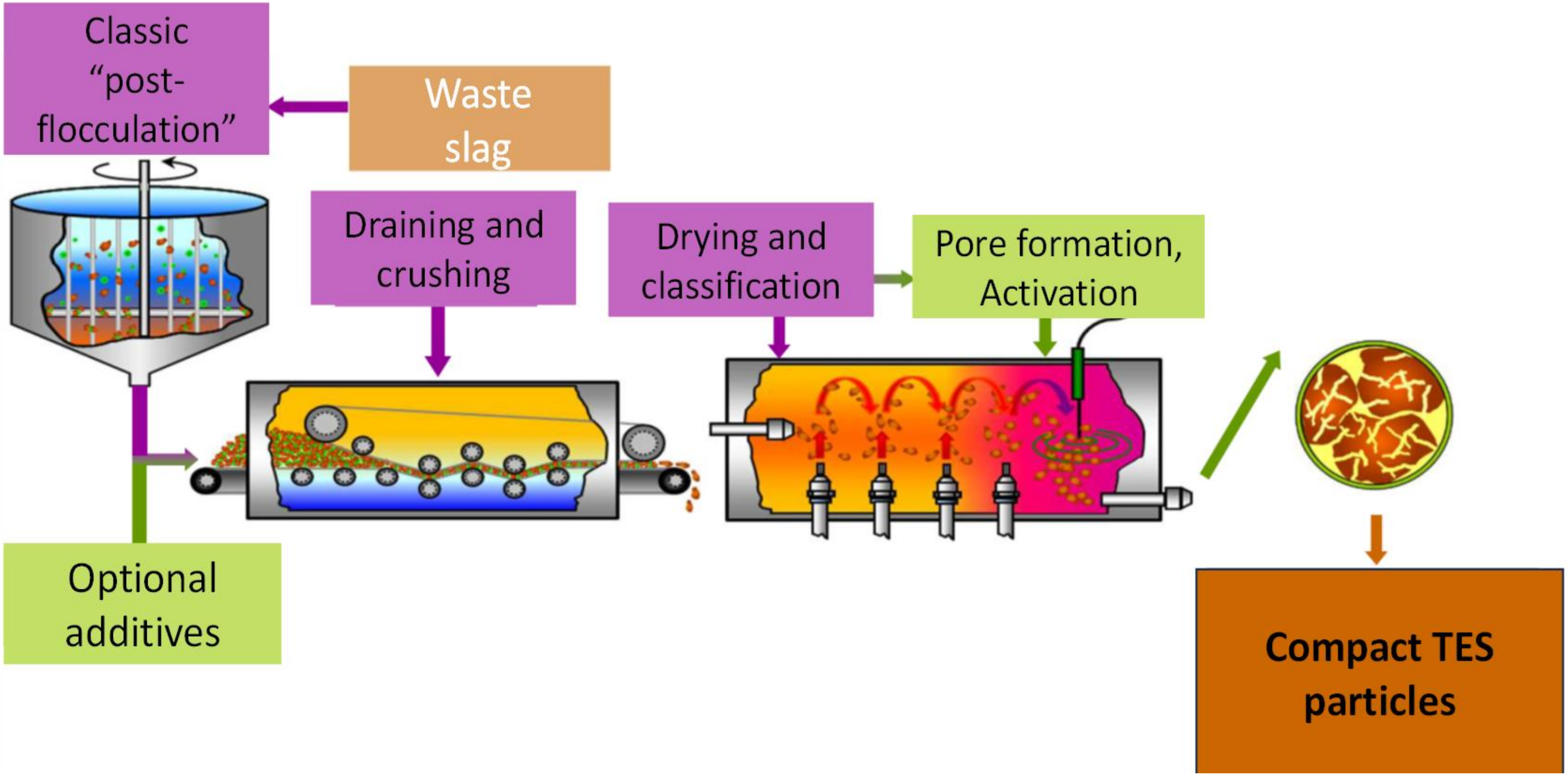
Processing of industrial slag to TES particles



Classic "post-flocculation"

Waste slag

Draining and crushing

Drying and classification

Pore formation, Activation

Optional additives

Compact TES particles

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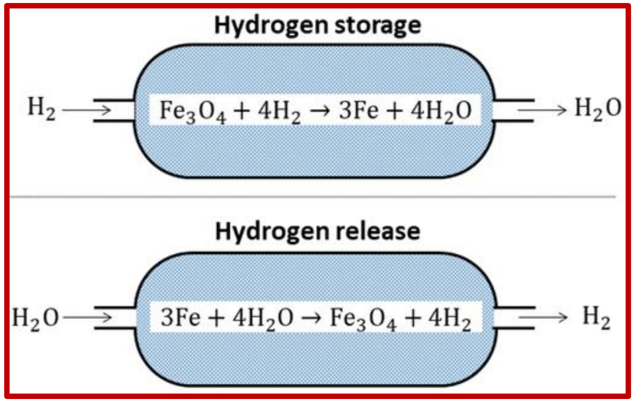
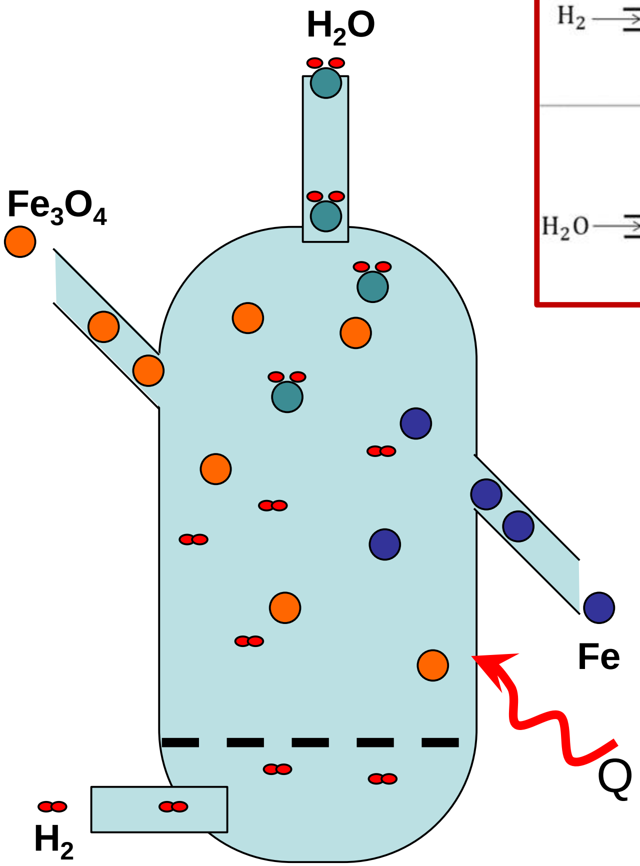
Thermochemical hydrogen storage: Redox reactions

Redox reactor

- *Continuous operation*

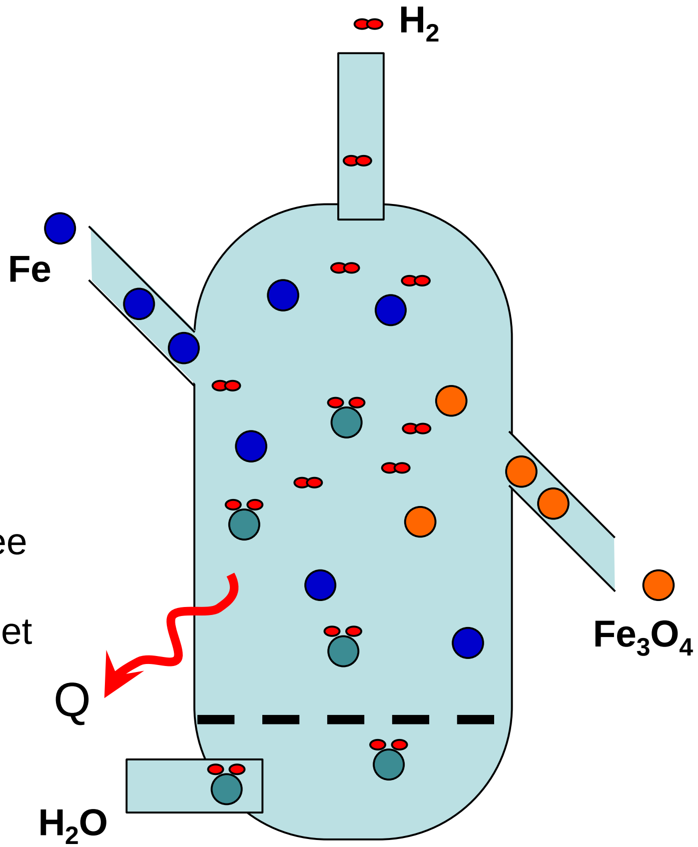




Storage H_2

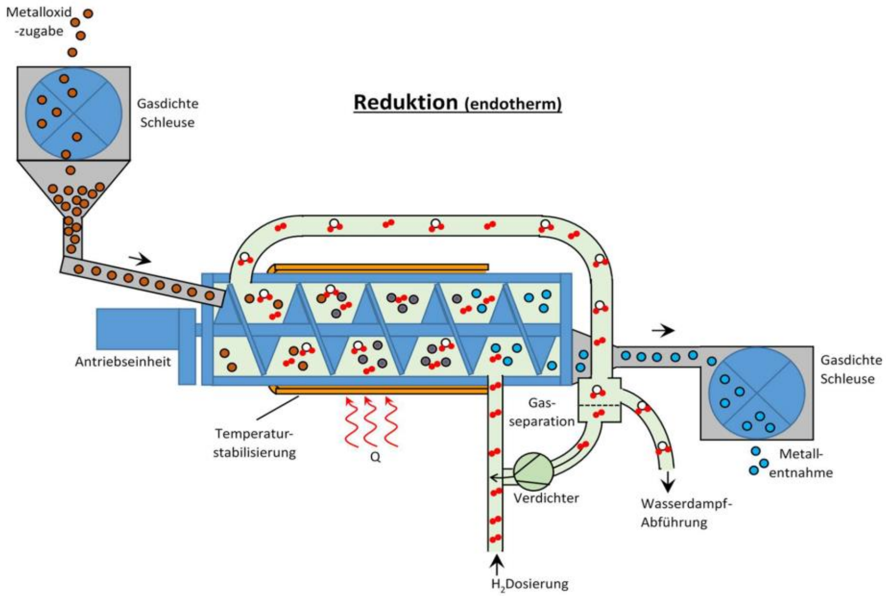
Requirements:

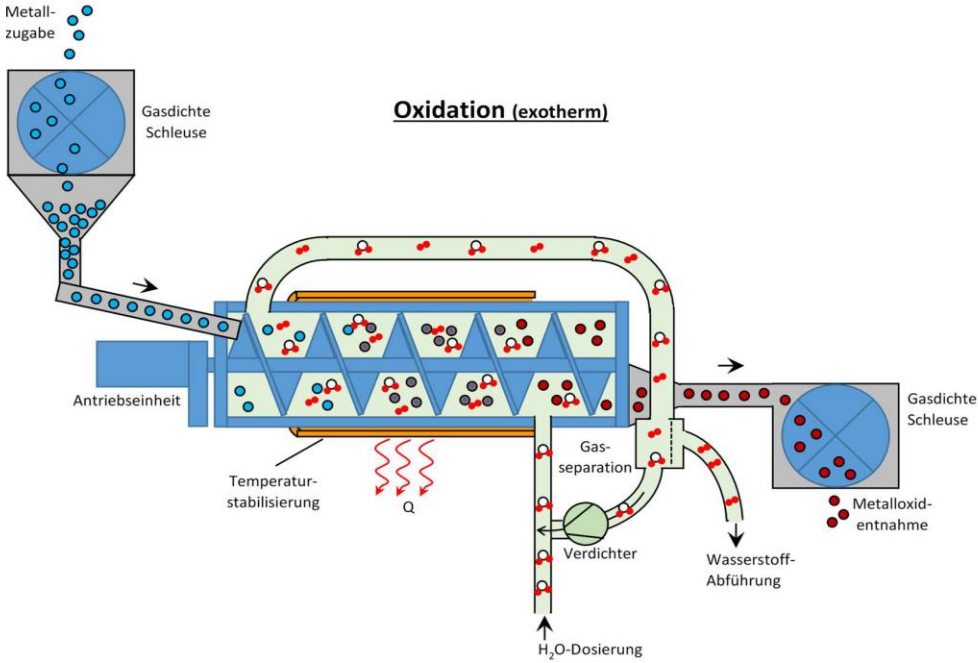
- Low-/reduced-abrasion free conveying of solids
- Gas-tight solid and gas inlet and outlet

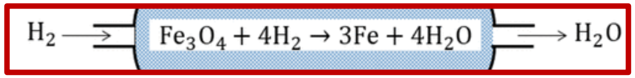


Release H_2

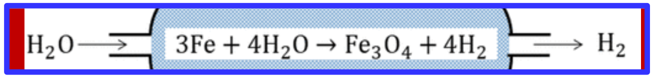
Thermochemical hydrogen storage: Redox reactions





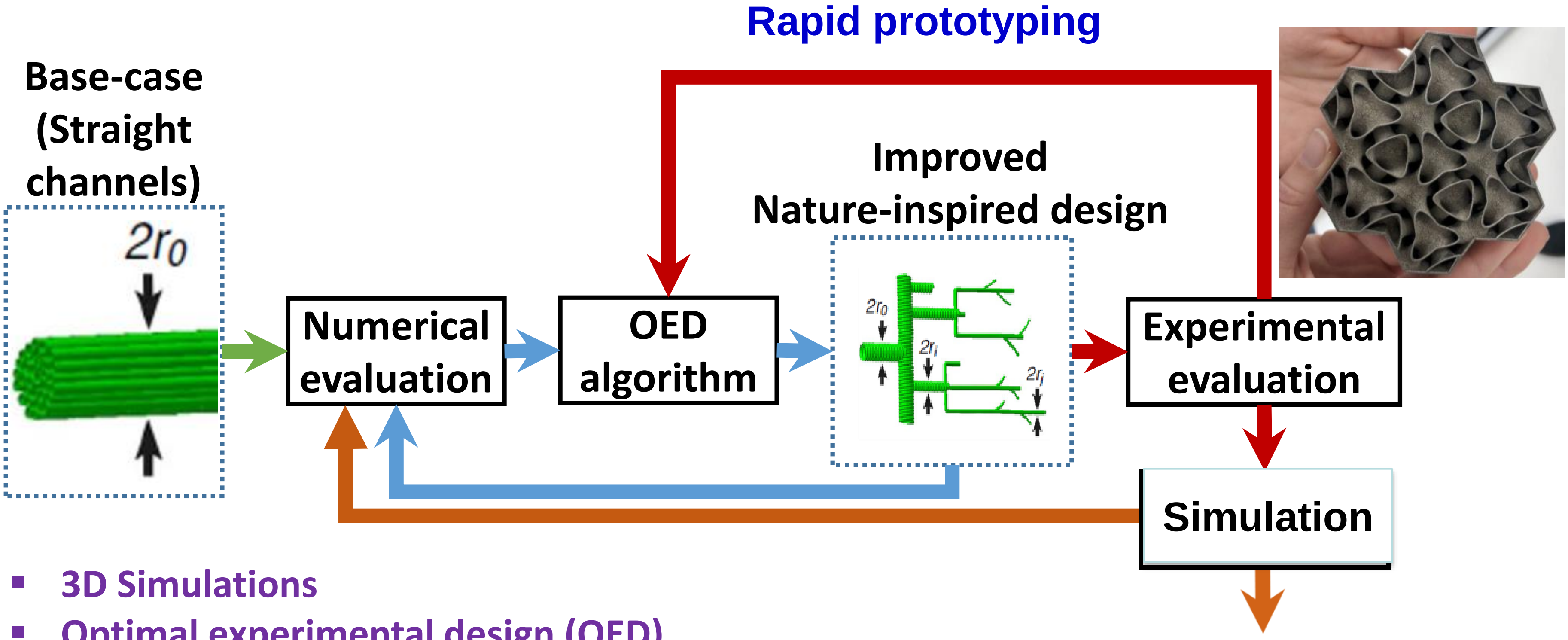


$$H_2 \rightarrow Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O \rightarrow H_2O$$



$$H_2O \rightarrow 3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \rightarrow H_2$$

Digitalization Framework



Rapid prototyping

Base-case (Straight channels)

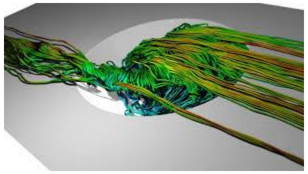
Numerical evaluation

OED algorithm

Improved Nature-inspired design

Experimental evaluation

Simulation



- 3D Simulations
- Optimal experimental design (OED)
- Machine learning / Data analytics
- 3D printing / additive manufacturing
- Material design
- Digital twin

“You cannot solve a problem with the same mind that created it”

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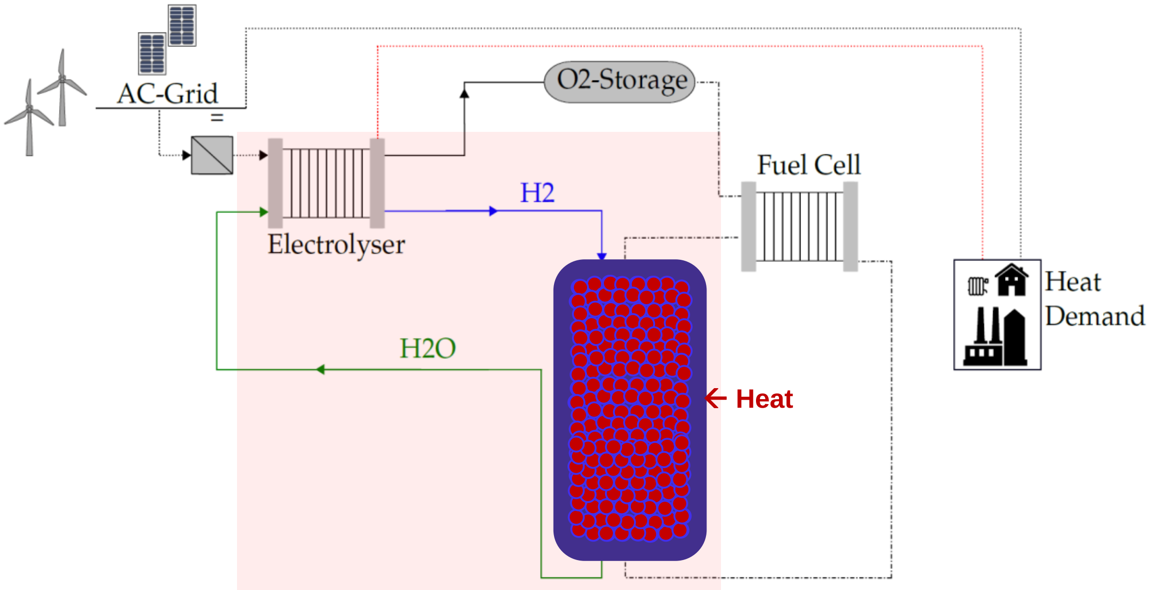
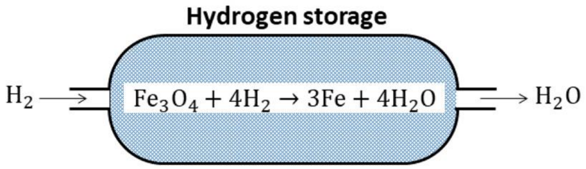
Thermochemical hydrogen storage: Redox reactions

Charging phase



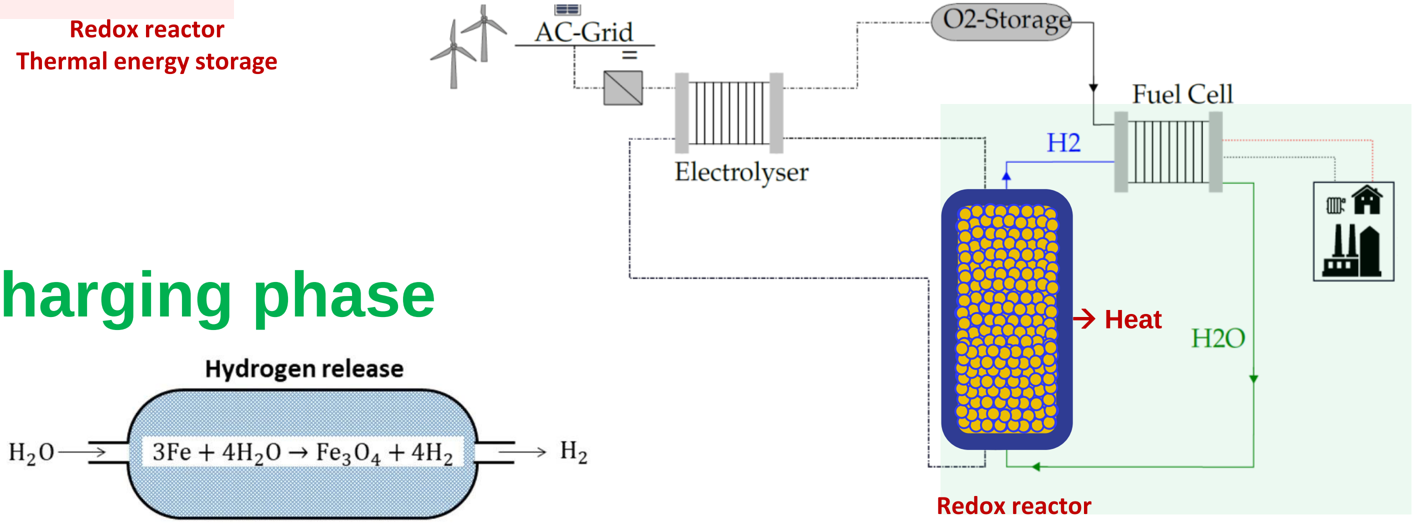
Redox reactor
Thermal energy storage

Hydrogen storage



$$H_2 \rightarrow \quad Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O \quad \rightarrow H_2O$$

Discharging phase



$$H_2O \rightarrow \quad 3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \quad \rightarrow H_2$$

Redox reactor
Thermal energy storage

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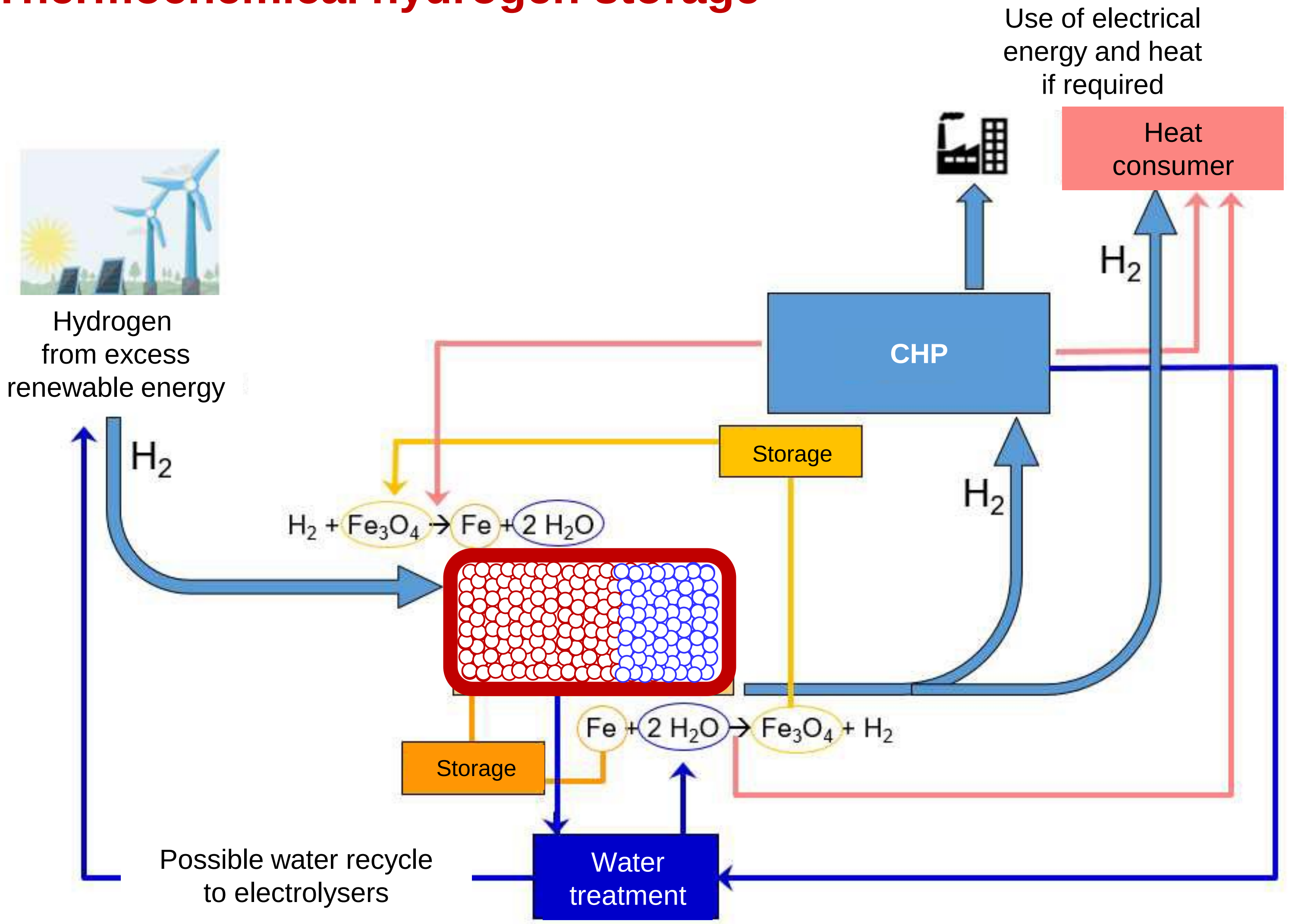
Energy storage

❑ Thermochemical hydrogen storage



Restricted/ Prohibited use and/or distribution of this material

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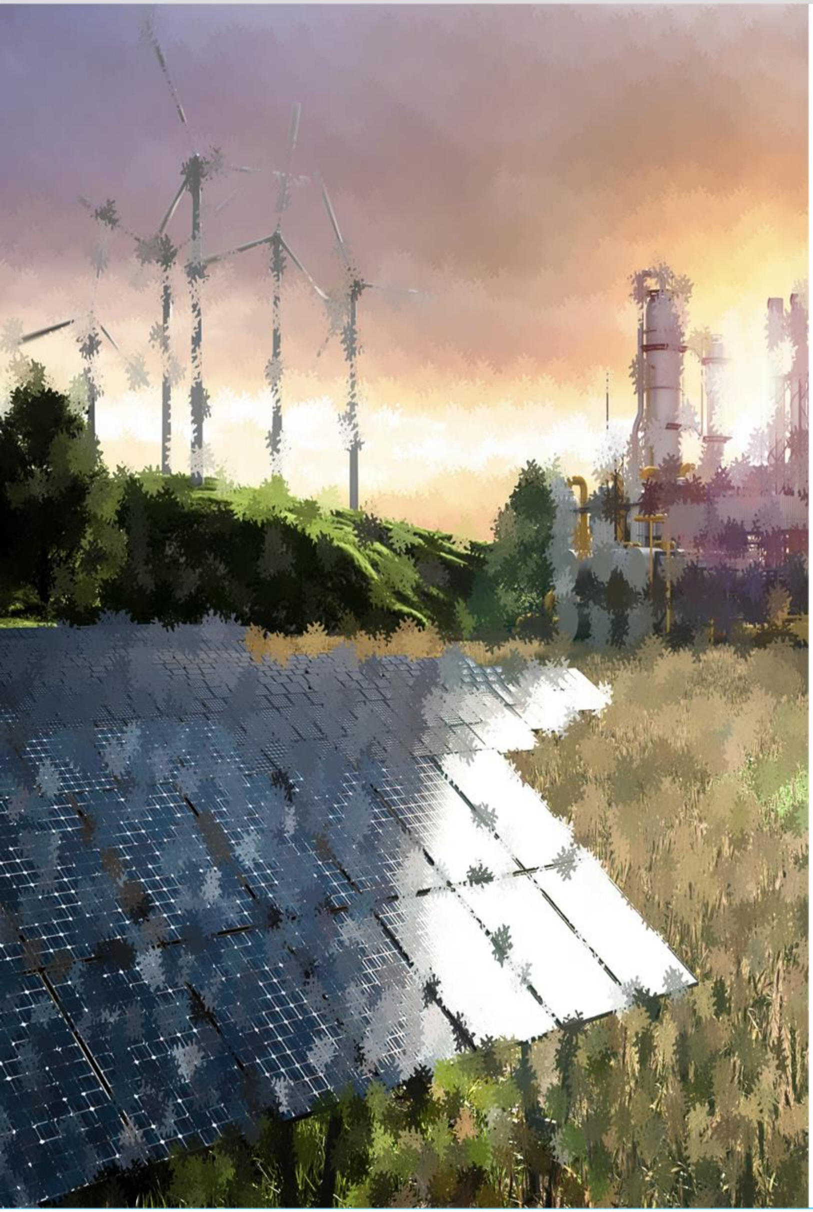
Outline

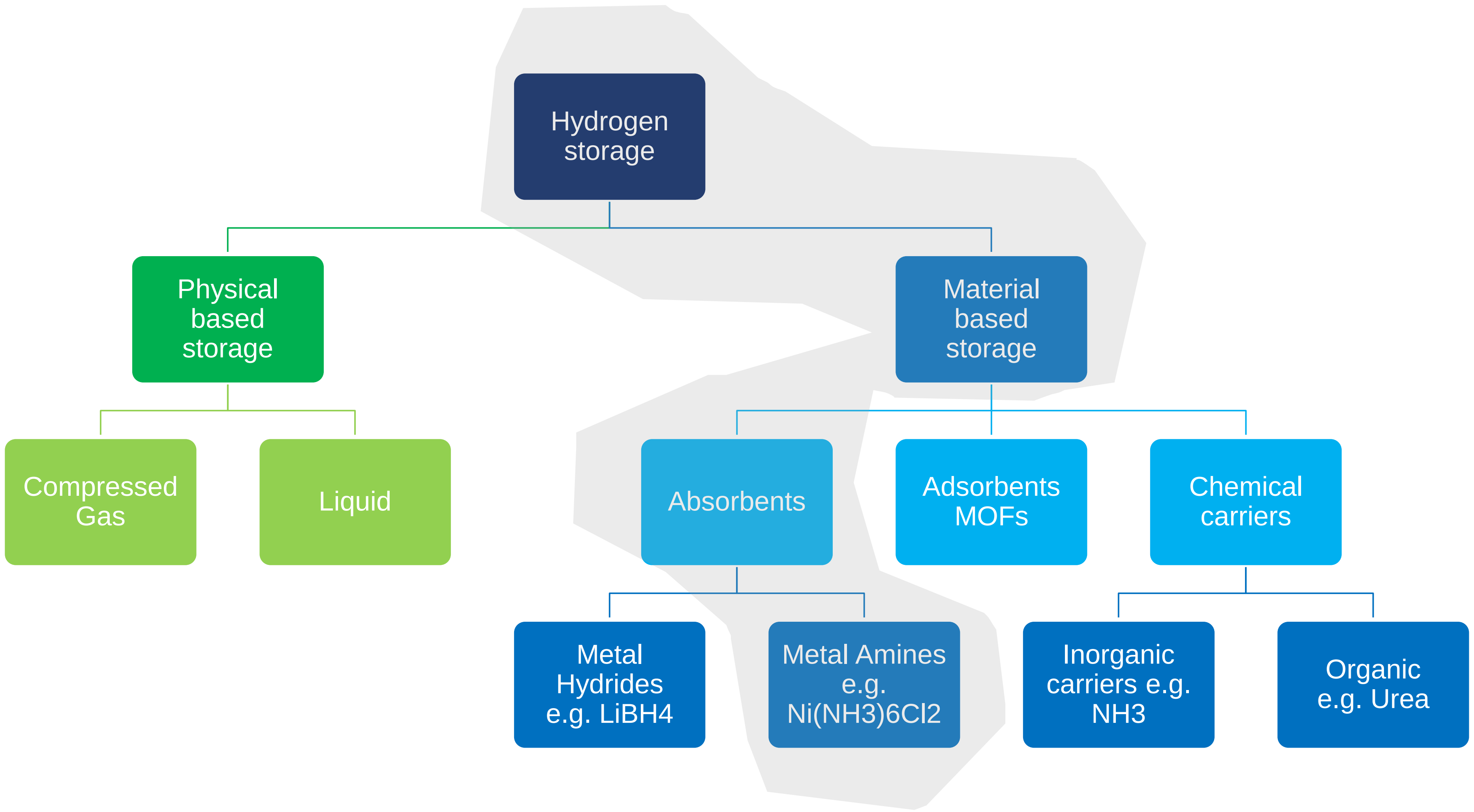


From sunlight and desert sand to a sustainable society

Thermochemical hydrogen storage: Redox reactor

Energy storage as metal ammine complexes

Hydrogen storage


Hydrogen storage

Physical based storage

Compressed Gas

Liquid

Material based storage

Absorbents

Metal Hydrides e.g. LiBH4

Metal Amines e.g. Ni(NH3)6Cl2

Adsorbents MOFs

Chemical carriers

Inorganic carriers e.g. NH3

Organic e.g. Urea

https://doi.org/10.1016/B978-0-443-15274-0.50472-8

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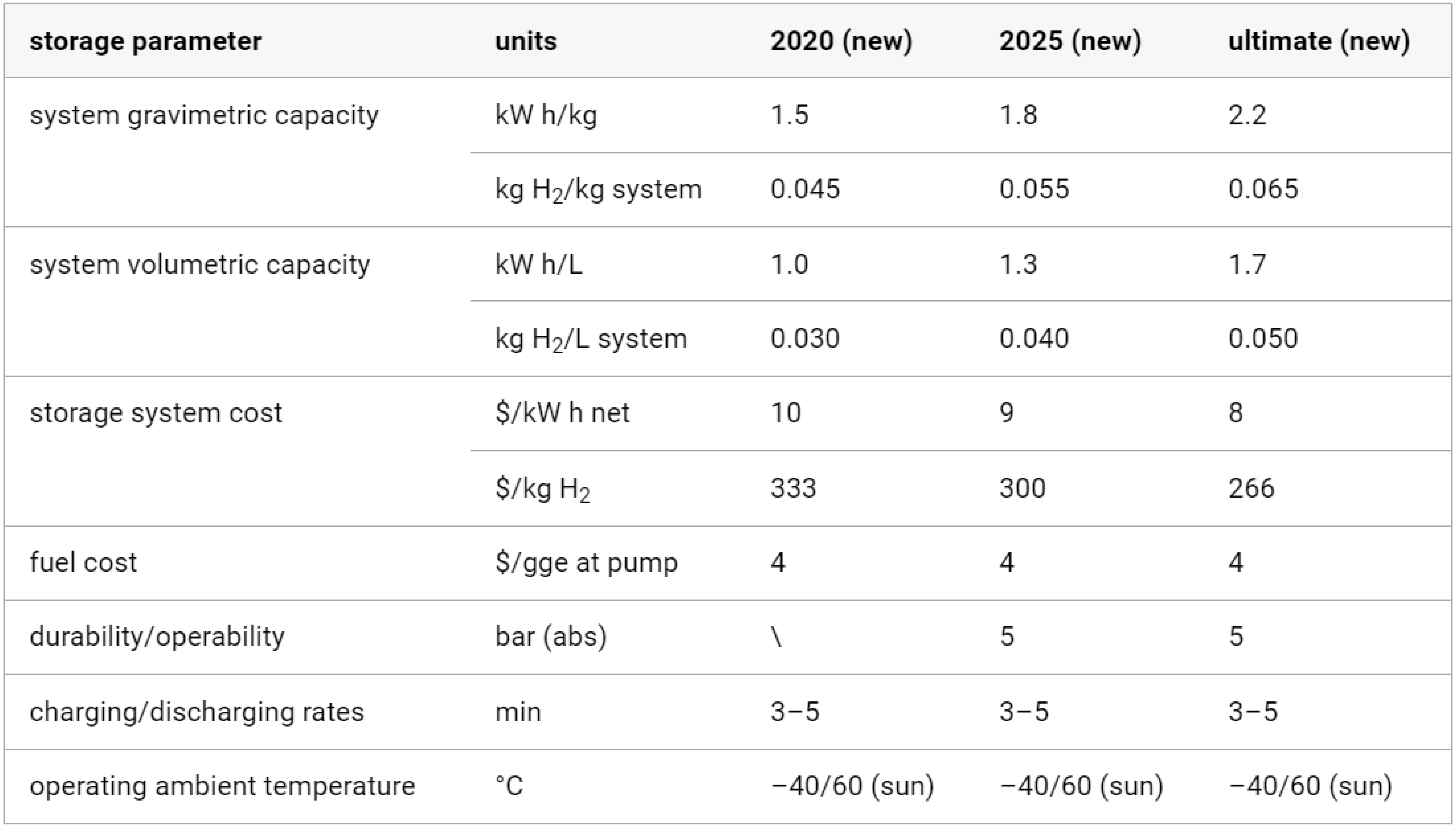
US DOE targets for hydrogen storage



storage parameter	units	2020 (new)	2025 (new)	ultimate (new)
system gravimetric capacity	kW h/kg	1.5	1.8	2.2
	kg H_2/kg system	0.045	0.055	0.065
system volumetric capacity	kW h/L	1.0	1.3	1.7
	kg H_2/L system	0.030	0.040	0.050
storage system cost	$/kW h net	10	9	8
	$/kg H_2	333	300	266
fuel cost	$/gge at pump	4	4	4
durability/operability	bar (abs)	\	5	5
charging/discharging rates	min	3−5	3−5	3−5
operating ambient temperature	°C	−40/60 (sun)	−40/60 (sun)	−40/60 (sun)

https://doi.org/10.1021/acs.iecr.0c04387

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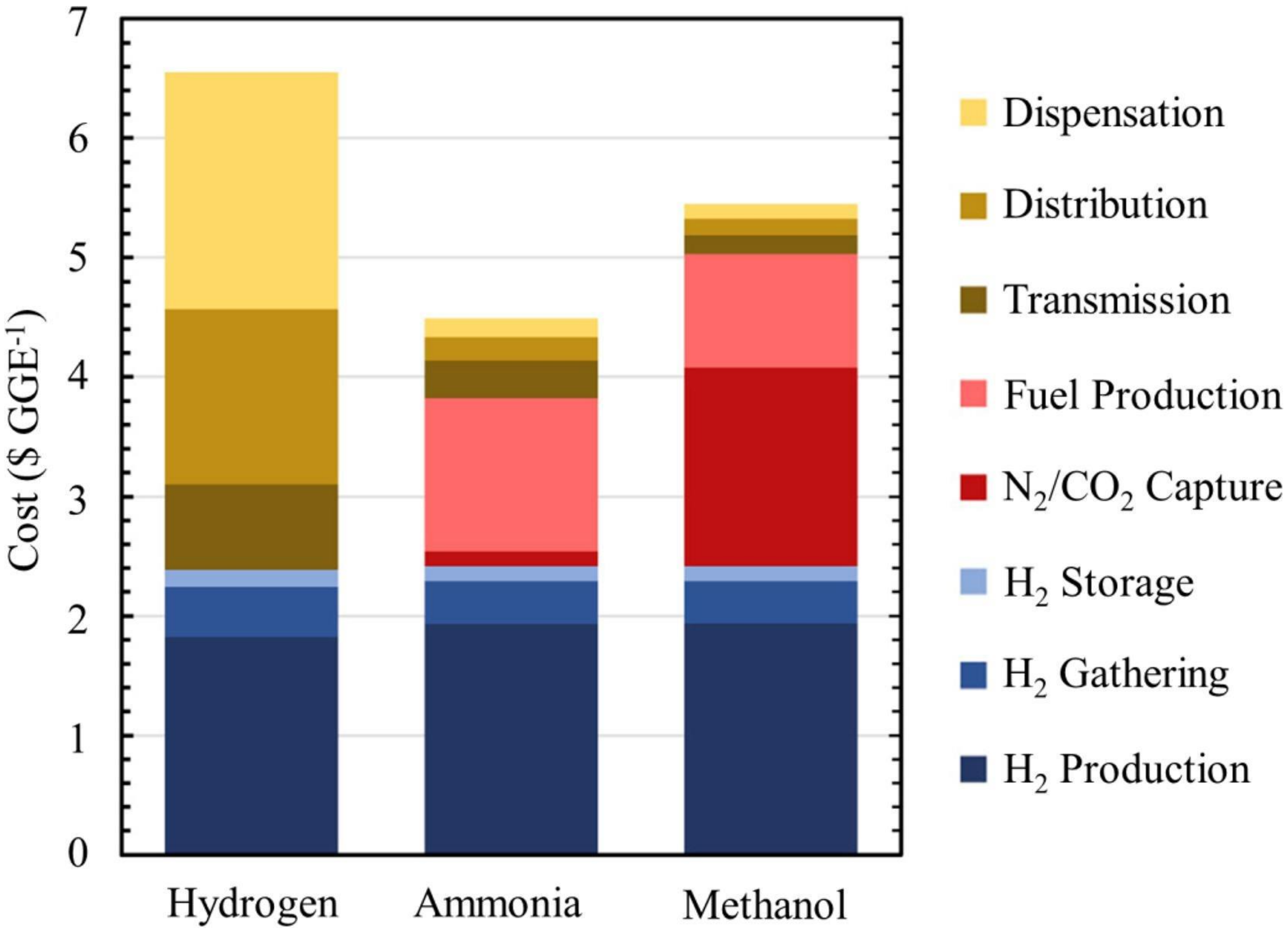
Ammonia vs. Hydrogen



https://doi.org/10.1016/j.enconman.2020.113729

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Ammonia vs. Hydrogen

Characteristics	Liquid hydrogen	Ammonia
Molecular weight (g/mol)	2.016	17.03
Density (kg/m^3)	70.8	682
Boiling point (^{0}C)	-252.9	-33.34
Gravimetric H_2 density (wt %)	100	17.8
Volumetric H_2 density (kg H_2/m^3)	70.9	**120.3**
Gravimetric energy density (MJ/kg)	120	21.18
Volumetric energy density (MJ/l)	8.49	**14.40**
H_2 release temperature (^{0}C)	-252.9	350 – 900
Regeneration temperature (^{0}C)	-	400 – 600
Ignition temperature (^{0}C)	571	651
Enthalpy change during H_2 release (kJ/mol)	0.899	30.6
Physical	High H_2 density ~ 800x volumetric H_2 density	**Very high H_2 density** **~1200x volumetric H_2 density**
Infrastructure	Needs further development for large scale	**Possible to utilize infrastructure currently available for propane**

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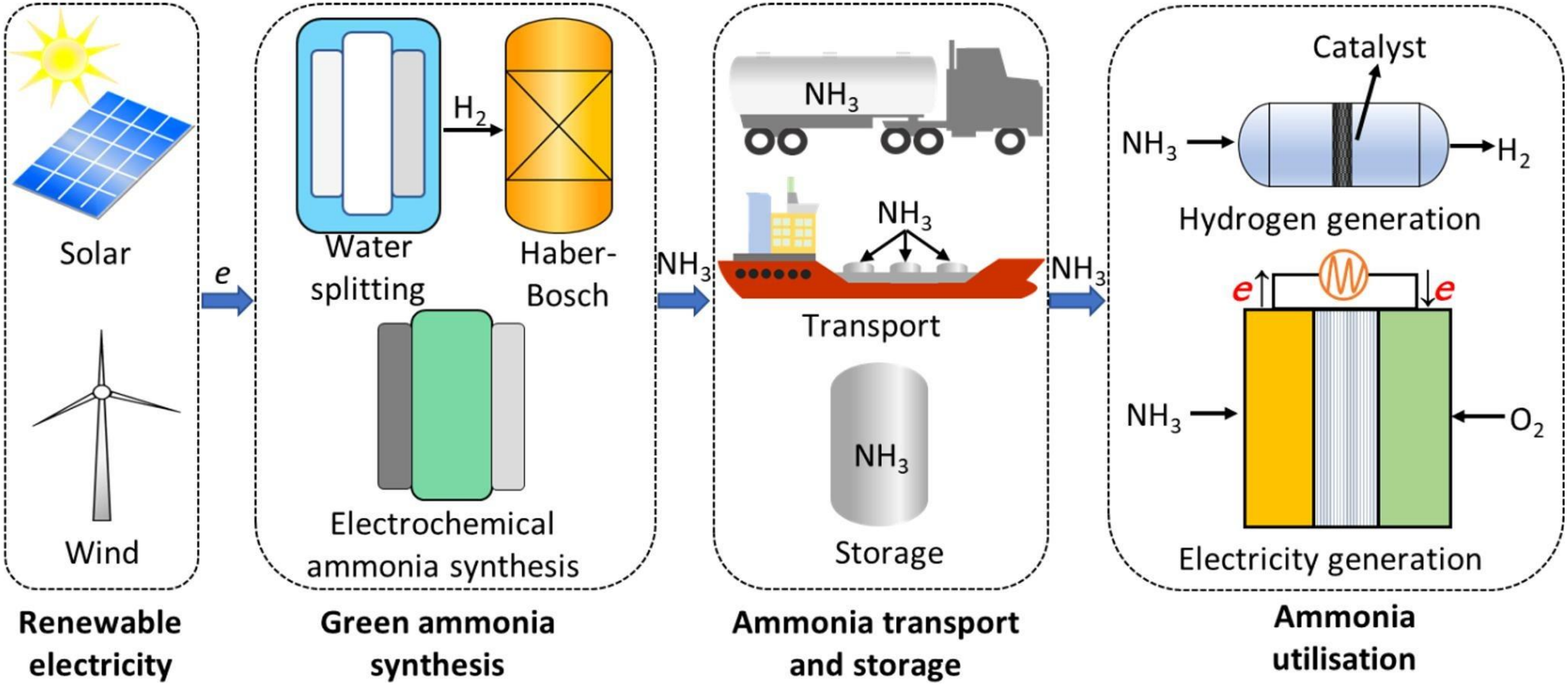
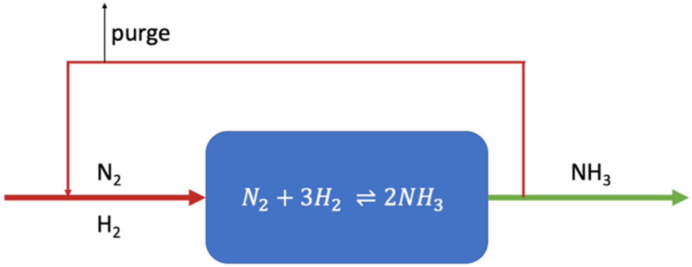
https://doi.org/10.1016/j.ijhydene.2019.04.112

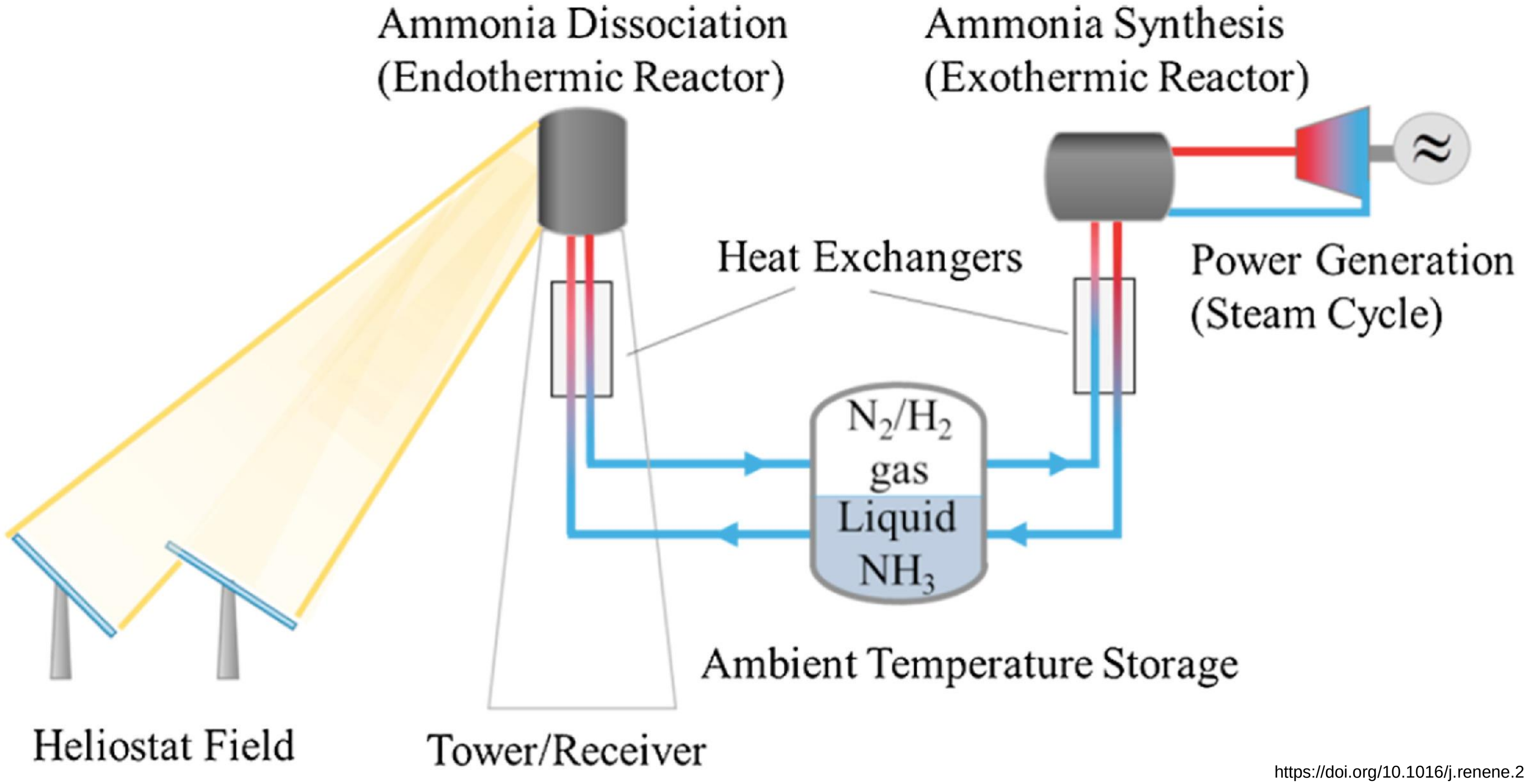
System integration



https://doi.org/10.1016/j.enconman.2020.113729

Ammonia-based thermochemical energy storage





https://doi.org/10.1016/j.renene.2022.06.015

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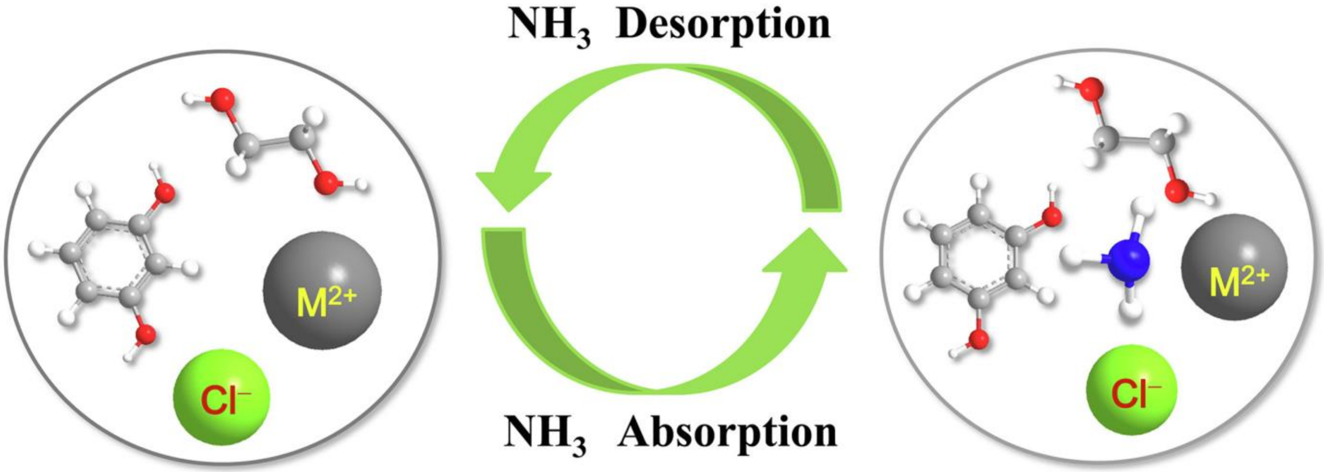
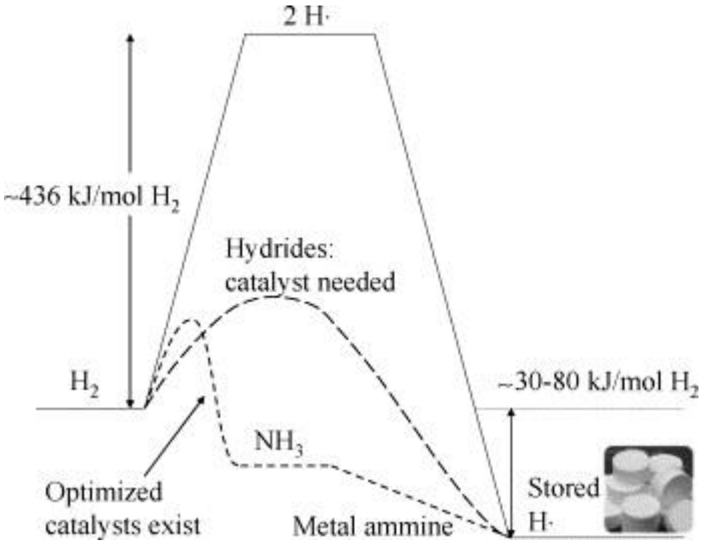
Energy storage as metal ammine complexes





https://doi.org/10.1016/j.ijhydene.2022.03.101
https://doi.org/10.1016/j.cattod.2005.10.011

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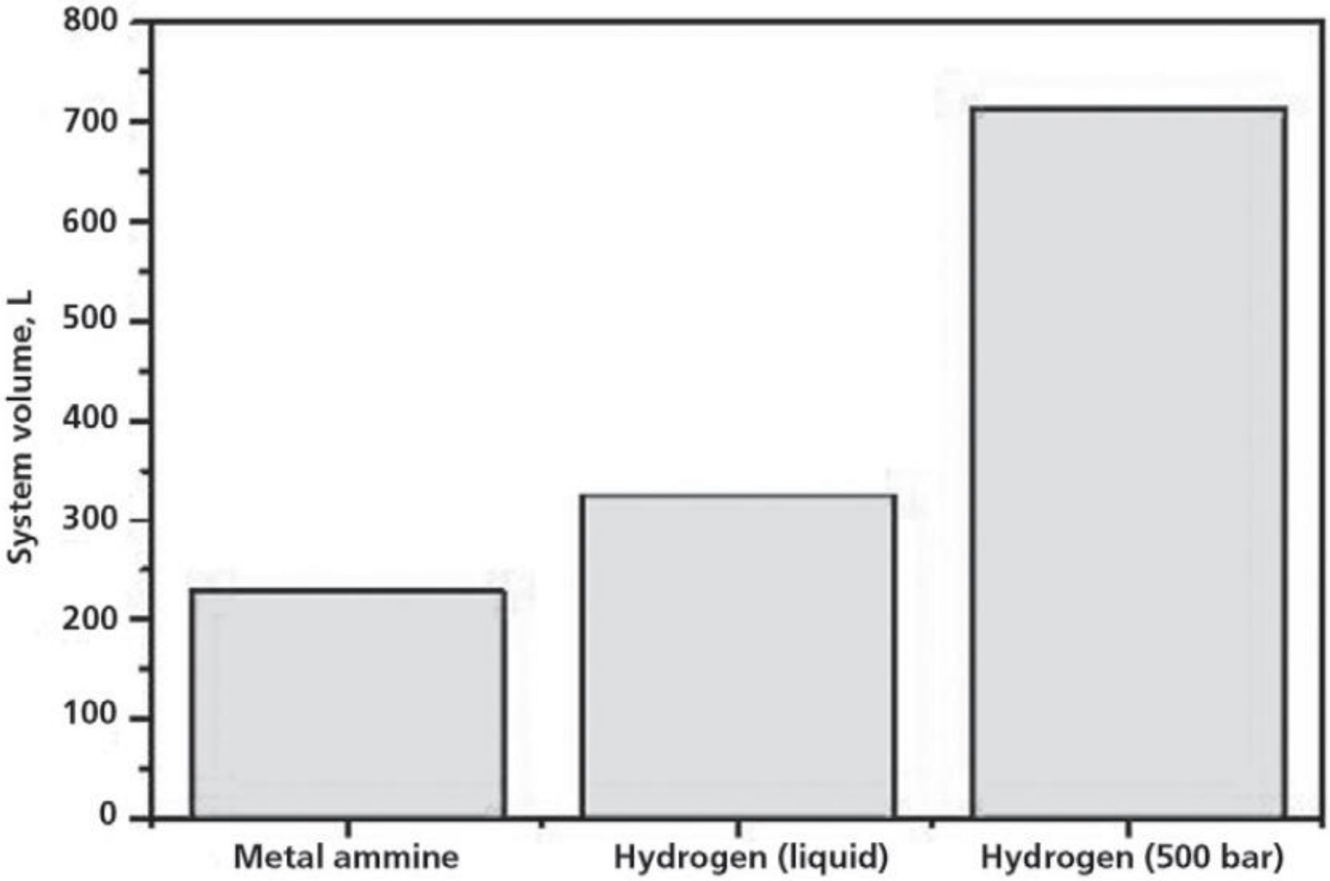
Energy storage as metal ammine complexes



https://doi.org/10.1016/S1464-2859(09)70336-0

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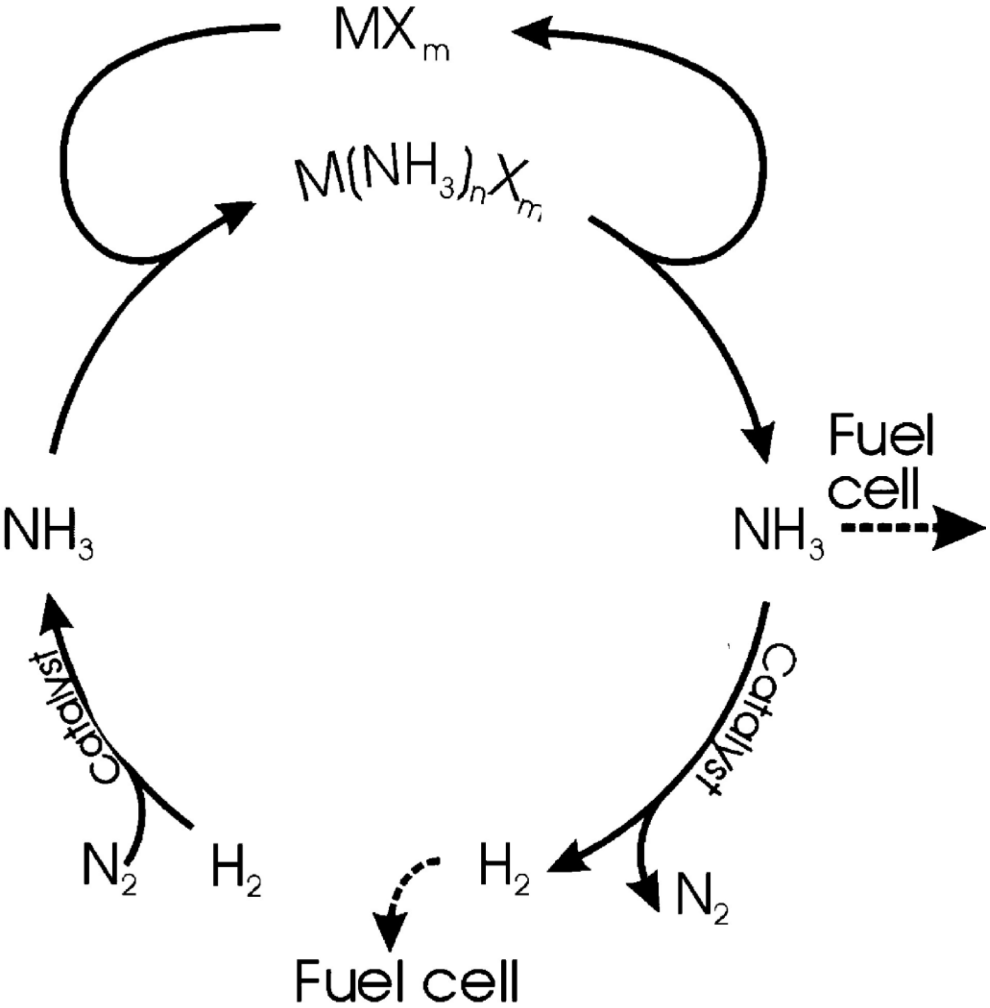
Energy storage as metal ammine complexes



https://doi.org/10.1021/ja076762c

https://doi.org/10.1039/B720020J

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Energy storage as metal ammine complexes

Metal halide	Metal ammine complex	Plateau pressure (bar)	Theoretical gravimetric NH_3 density	Standard enthalpy change (kJ/mol NH_3)
$LiCl$	$Li(NH_3)_4Cl$	1.78	61.6	-34.0
NaI	$Na(NH_3)_5I$	0.55	36.2	-
$MgCl_2$	$Mg(NH_3)Cl_2$	6.45e-09	15.2	-87.0
	$Mg(NH_3)_2Cl_2$	8.04e-07	26.3	-74.8
	$Mg(NH_3)_6Cl_2$	5.00e-03	51.8	-55.6
$MnBr_2$	$Mn(NH_3)Br_2$	2.36e-07	7.3	-83.7
	$Mn(NH_3)_3Br_2$	2.77e-06	13.7	-77.0
	$Mn(NH_3)_6Br_2$	0.03	32.2	-53.1
$NiCl_2$	$Ni(NH_3)_6Cl_2$	**6.00e-04**	**44.1**	**-59.2**
NiI_2	$Ni(NH_3)_6I_2$	4.00e-04	24.6	-
$BaCl_2$	$Ba(NH_3)_8Cl_2$	1.27	39.6	-37.7

https://doi.org/10.1016/j.ijhydene.2020.01.145

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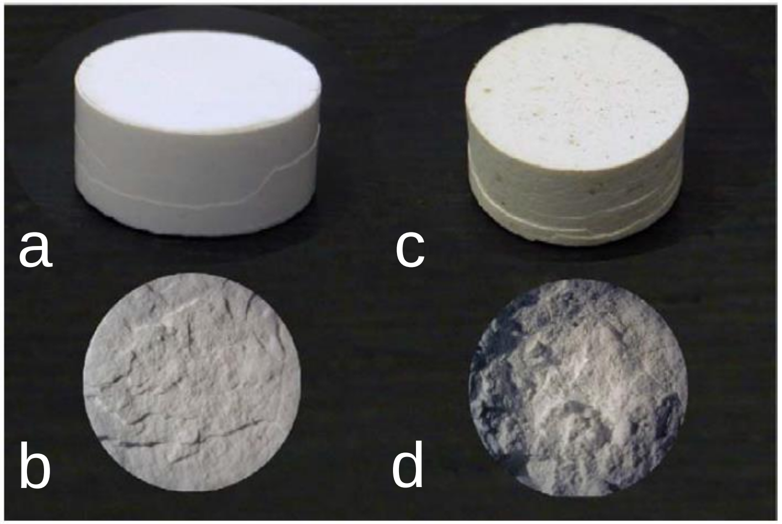
Energy storage as metal ammine complexes



$$Mg(NH_3)_6Cl_2$$

$$NiCl_2$$

$$Ni(NH_3)_6Cl_2$$

https://doi.org/10.1016/j.cattod.2005.10.011
https://doi.org/10.1021/ja076762c

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Material selection

Material	Stored component	Reaction	Hydrogen content (wt %)	Decomposition temperature (^{0}C)	
				Simulated	Literature
NH_4Cl	NH_3	$NH_4Cl \rightarrow NH_3 + HCl$	7.54	328	350
$Ca(NH_3)_8Cl_2$	NH_3	$Ca(NH_3)_8Cl_2 \rightarrow \cdots \rightarrow 8\ NH_3 + CaCl_2$	9.78	-	-
$Ni(NH_3)_6Cl_2$	**NH_3**	$\boldsymbol{Ni(NH_3)_6Cl_2 \rightarrow \cdots \rightarrow 6\ NH_3 + NiCl_2}$	**7.83**	**44**	**79-140**
NH_4HCO_3	NH_3	$NH_4HCO_3 \rightarrow NH_3 + H_2O + CO_2$	6.37	69	60
Urea	NH_3	$CO(NH_2)_2 \rightarrow HNCO + NH_3$	6.71	237	133
$LiBH_4$	H_2	$LiBH_4 \rightarrow LiH + B + 1{,}5\ H_2$	18.51	140	200

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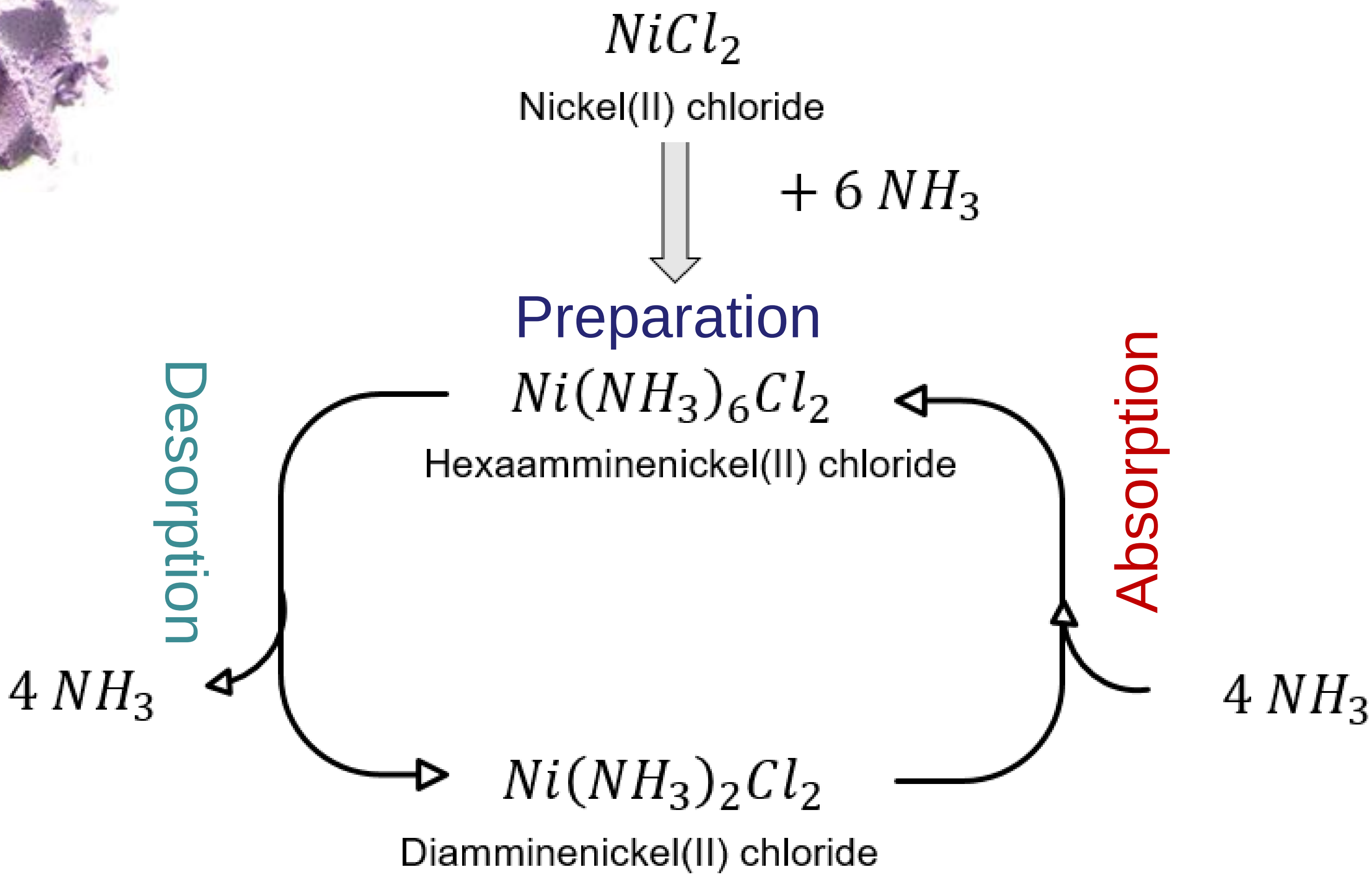
Reactions



$NiCl_2$

Nickel(II) chloride

$+ 6\ NH_3$

Preparation

$Ni(NH_3)_6Cl_2$

Hexaamminenickel(II) chloride

Desorption

Absorption

$4\ NH_3$

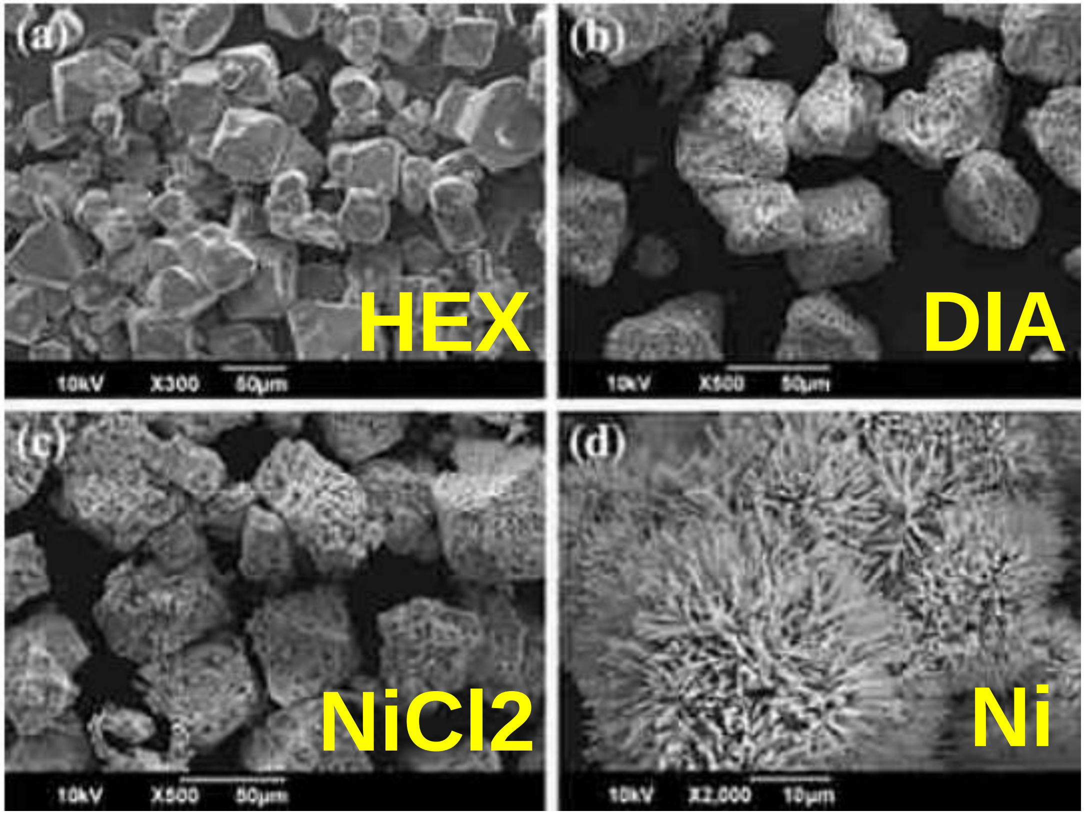
$4\ NH_3$

$Ni(NH_3)_2Cl_2$

Diamminenickel(II) chloride

https://doi.org/10.1021/ja076762c

Particle size distribution



50 µm

https://doi.org/10.1007/s10973-010-1054-8

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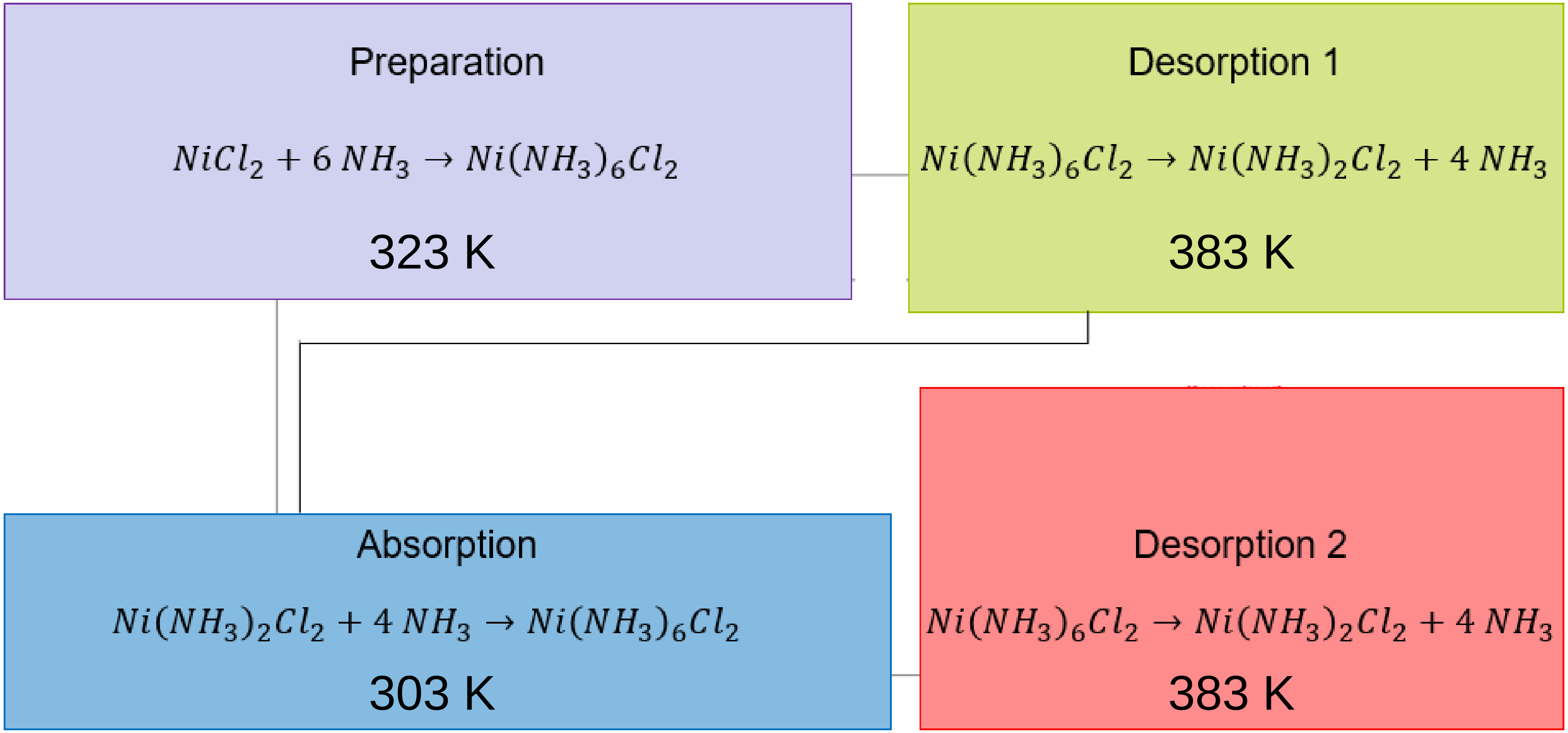
Proposed process concept



Preparation

$NiCl_2 + 6\,NH_3 \rightarrow Ni(NH_3)_6Cl_2$

323 K

Desorption 1

$Ni(NH_3)_6Cl_2 \rightarrow Ni(NH_3)_2Cl_2 + 4\,NH_3$

383 K

Absorption

$Ni(NH_3)_2Cl_2 + 4\,NH_3 \rightarrow Ni(NH_3)_6Cl_2$

303 K

Desorption 2

$Ni(NH_3)_6Cl_2 \rightarrow Ni(NH_3)_2Cl_2 + 4\,NH_3$

383 K

Cyclical storage and release of ammonia

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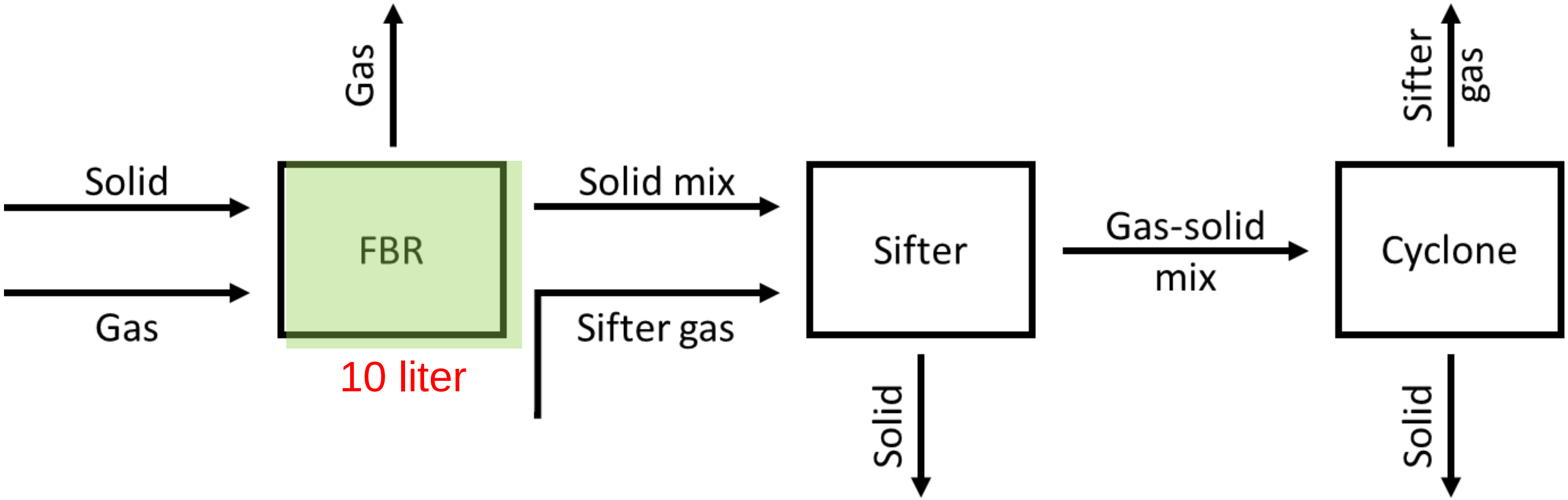
Proposed process concept



ADVANTAGES: High phase interface boundary
Uniform temperature
Easy transport of solids

SETUP: Fluidization behavior – based on density
Geometry – optimization (max. product, min. height)
Reactions – Power law utilizing known kinetics

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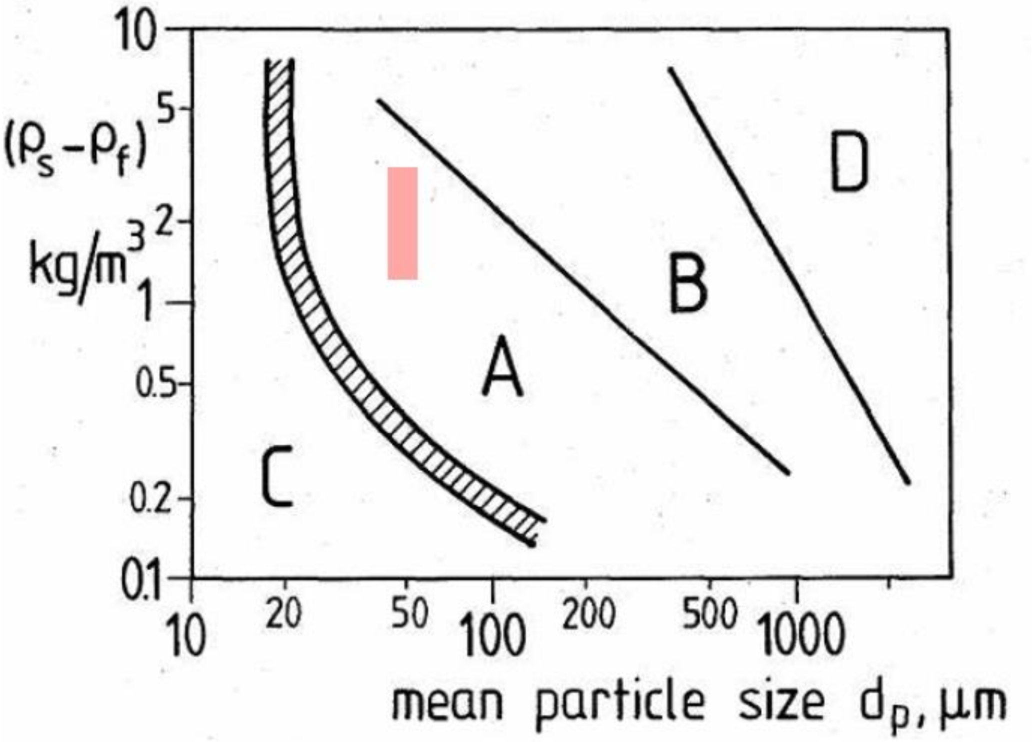
Fluidization behaviour

Material	Density (kg/m³)
NH_3	0.638
$NiCl_2$	3550
DIA	2310
HEX	1468



🟥 **Location of the present gas-solids combination**

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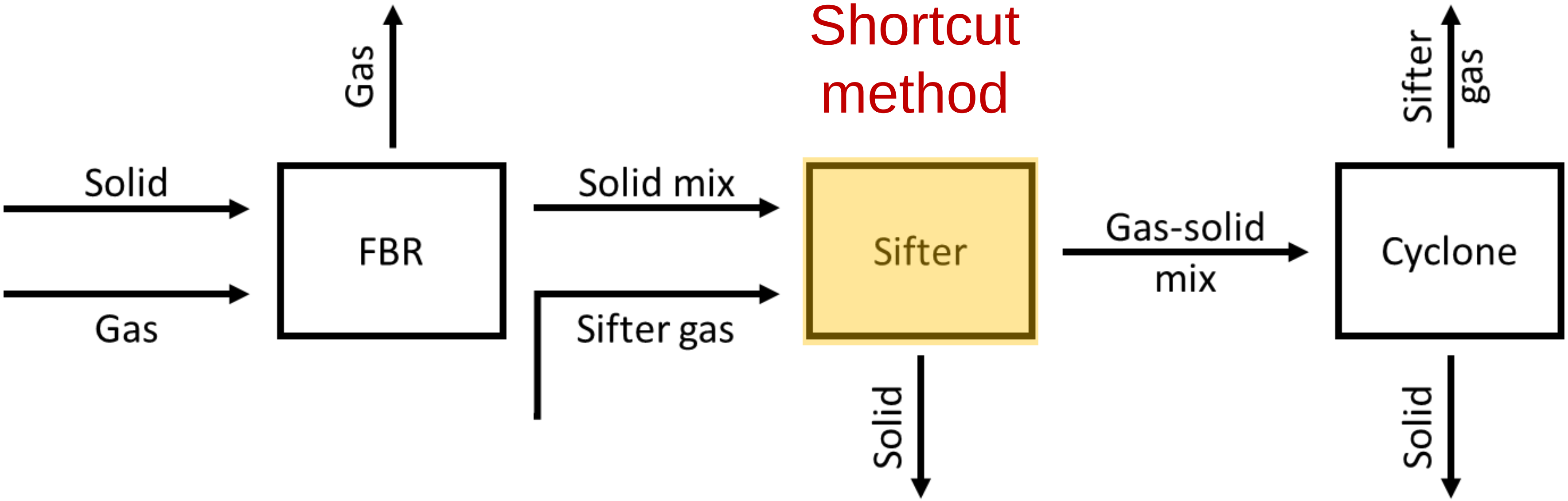
Separation



ADVANTAGES: Can separate based on density (real life)
No moving parts

SETUP: Detailed model not working ↔ shortcut method (cut density)
Sifter gas – optimization

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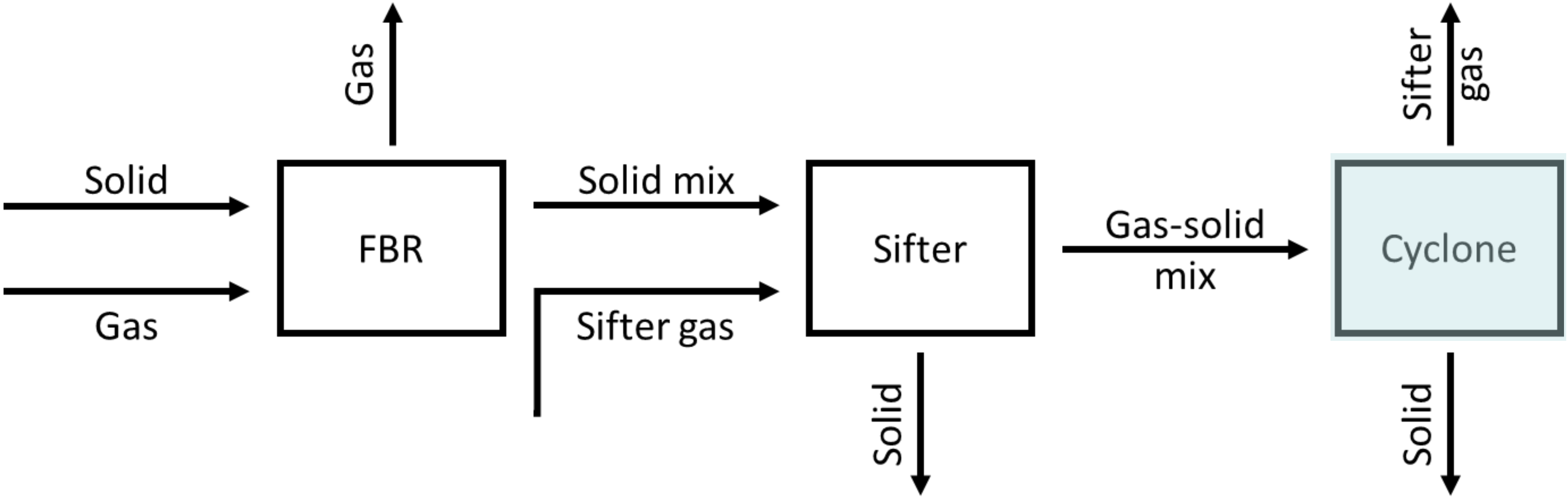
Separation



ADVANTAGES:	Simple structure No moving parts Low investment cost
SETUP:	Basic geometry

Standard calculation method (Muschelknautz)

Additional units

Equipment	Function	Specification
Mixer (solid)	Mixing excess educt with initial inlet stream	-
Mixer (gas)	Mixing excess ammonia with initial gas stream	Regulated by design specification to ensure constant gas flow at the start of simulation
Splitter	Removing released ammonia not needed for fluidization	Fixed flowrate for recycled ammonia
Compressor	Repressurizing ammonia stream after recycling	Isentropic compression to 1 bar outlet pressure

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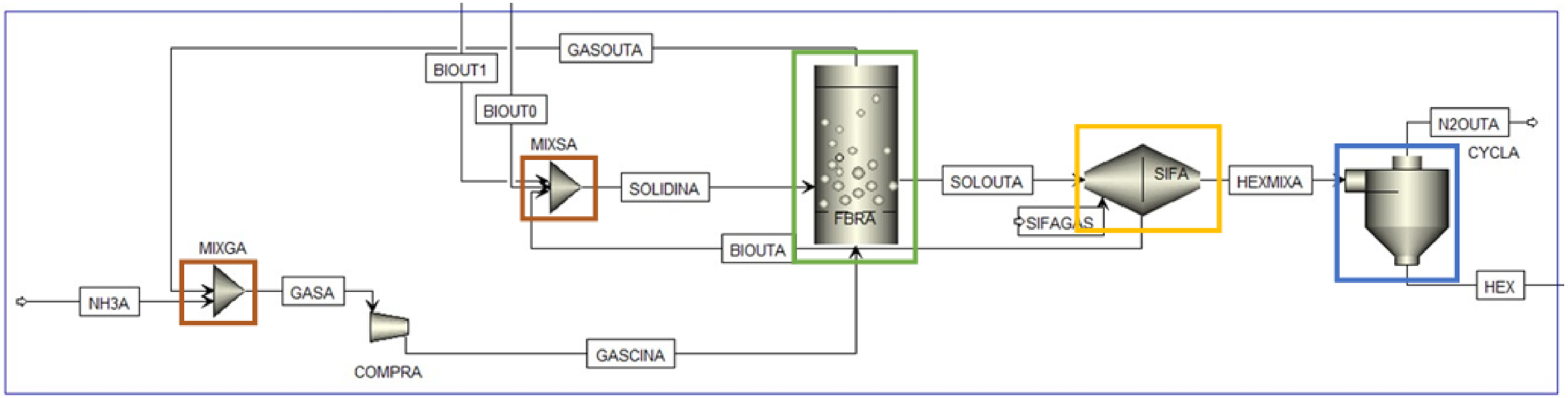
Process concept single stage



Mixer

Fluidized bed reactor

Sifter

Cyclone

:|

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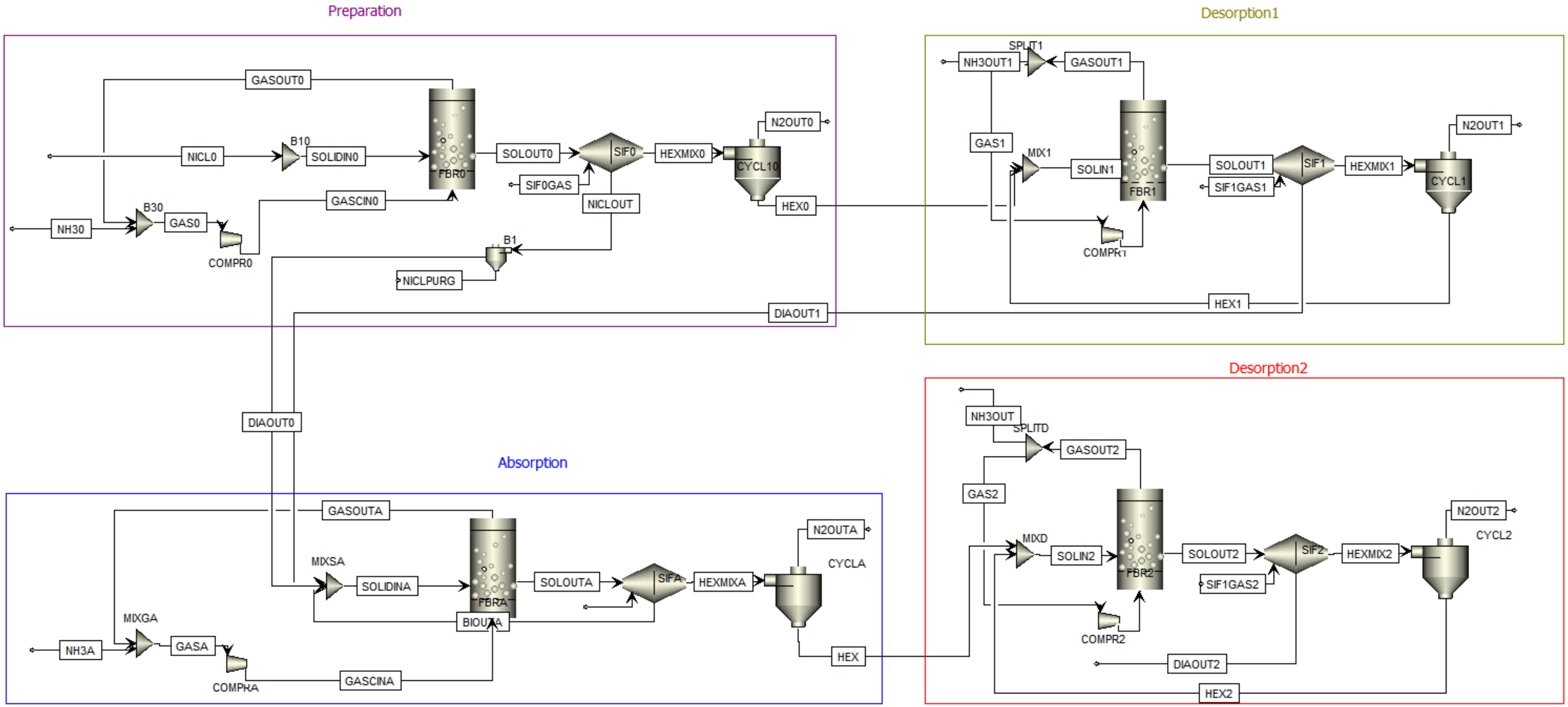
Process concept



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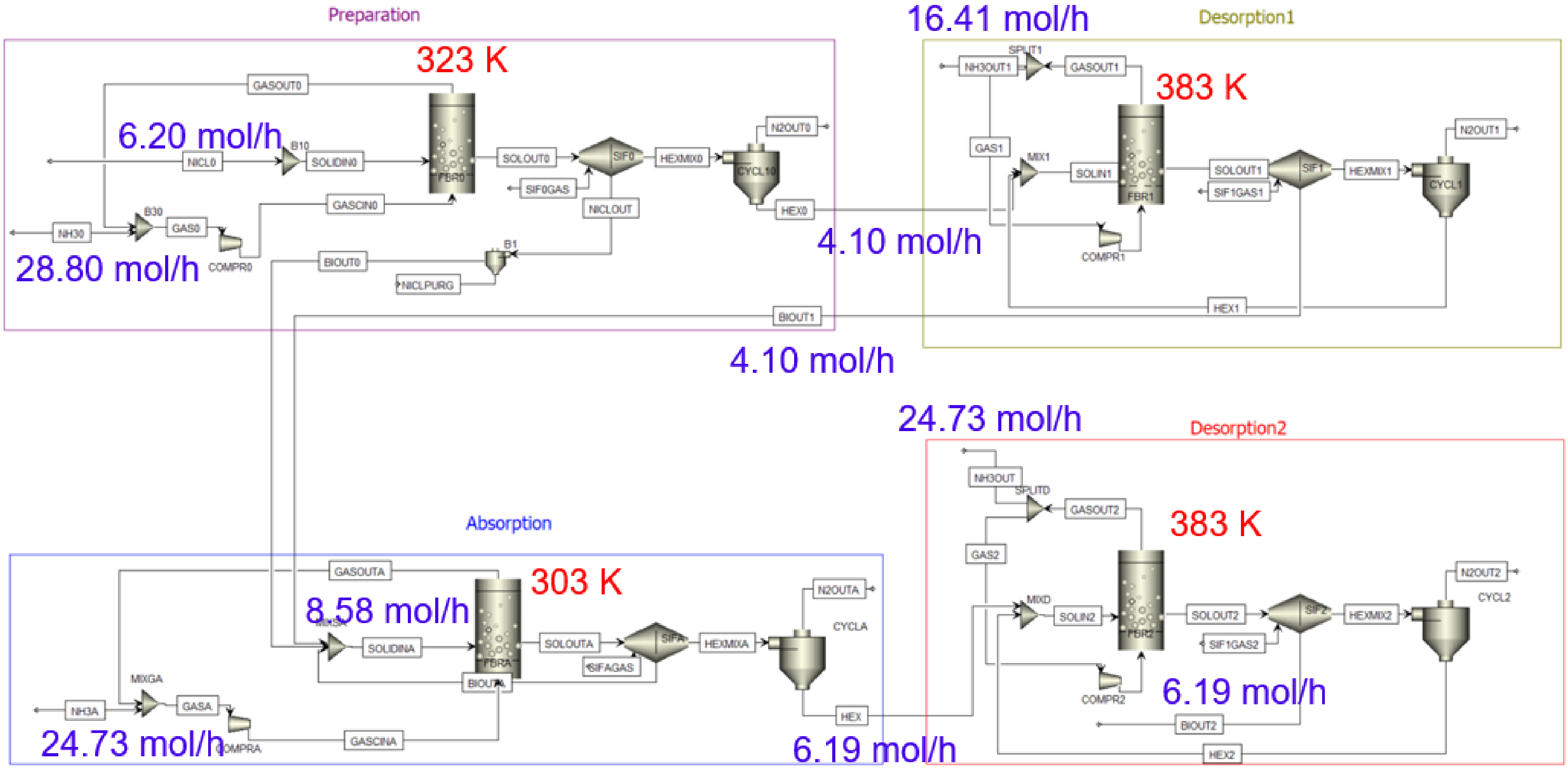
Steady state summary



Operation: Temperatures < 120 ^{0}C

Pressures < 1 bar

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US DOE targets for hydrogen storage

Parameter	Unit	Target	Proposed (preliminary)
Gravimetric hydrogen density	wt. %	> 4.5	**9.3**
Decomposition temperature	^{0}C	Low	< 120
Reusability		High	✓
Safety		Non-hazardous	✓
Production cost	$/kg H2	333	TBD

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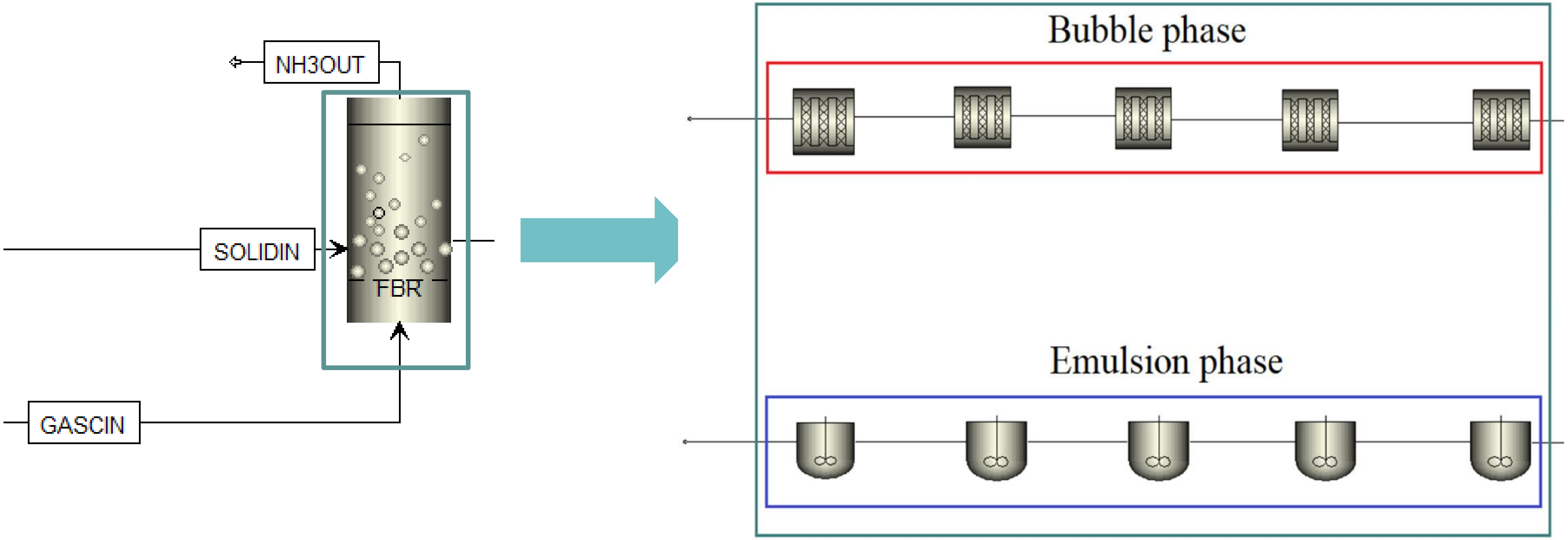
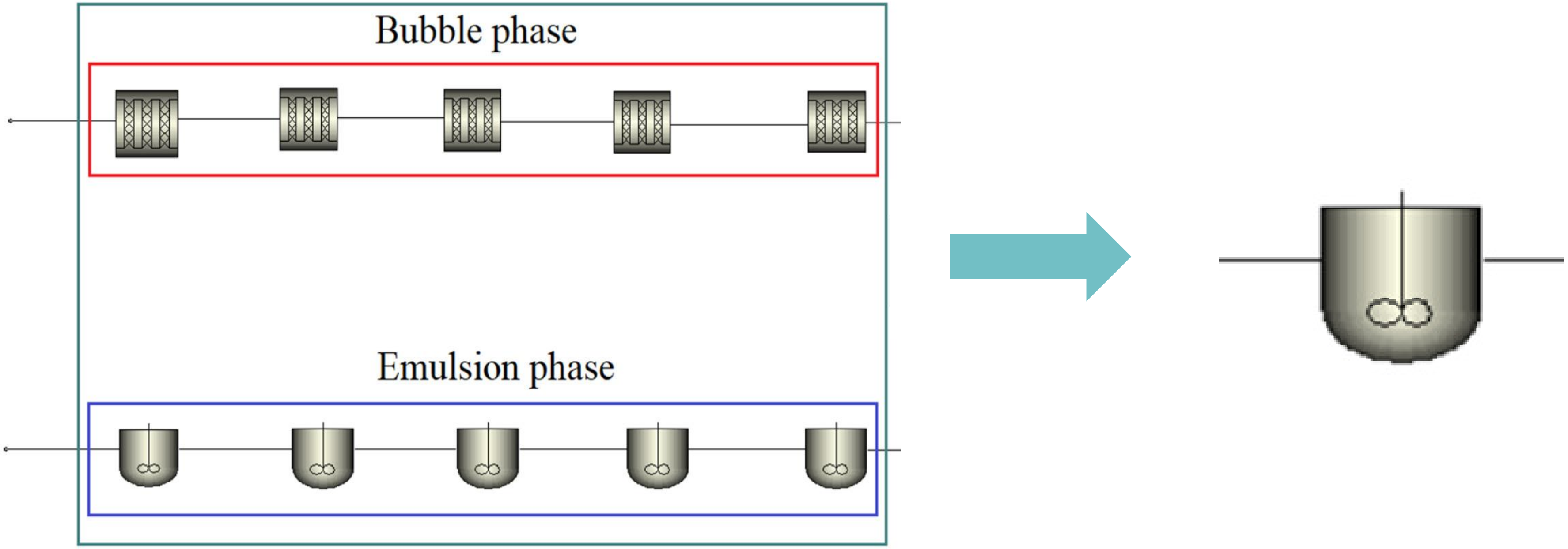
Towards dynamic simulation



FBR

Towards dynamic simulation



FBR

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Current work

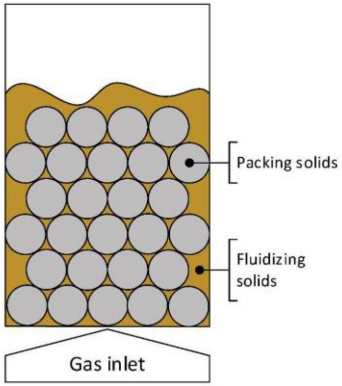
Brandenburg
University of Technology
Cottbus - Senftenberg

Dynamic simulations to assess

- System stability
- Start-up & shut-down of the various cycles of storage and release
- Control strategies

Optimization of the operation

Cost analysis



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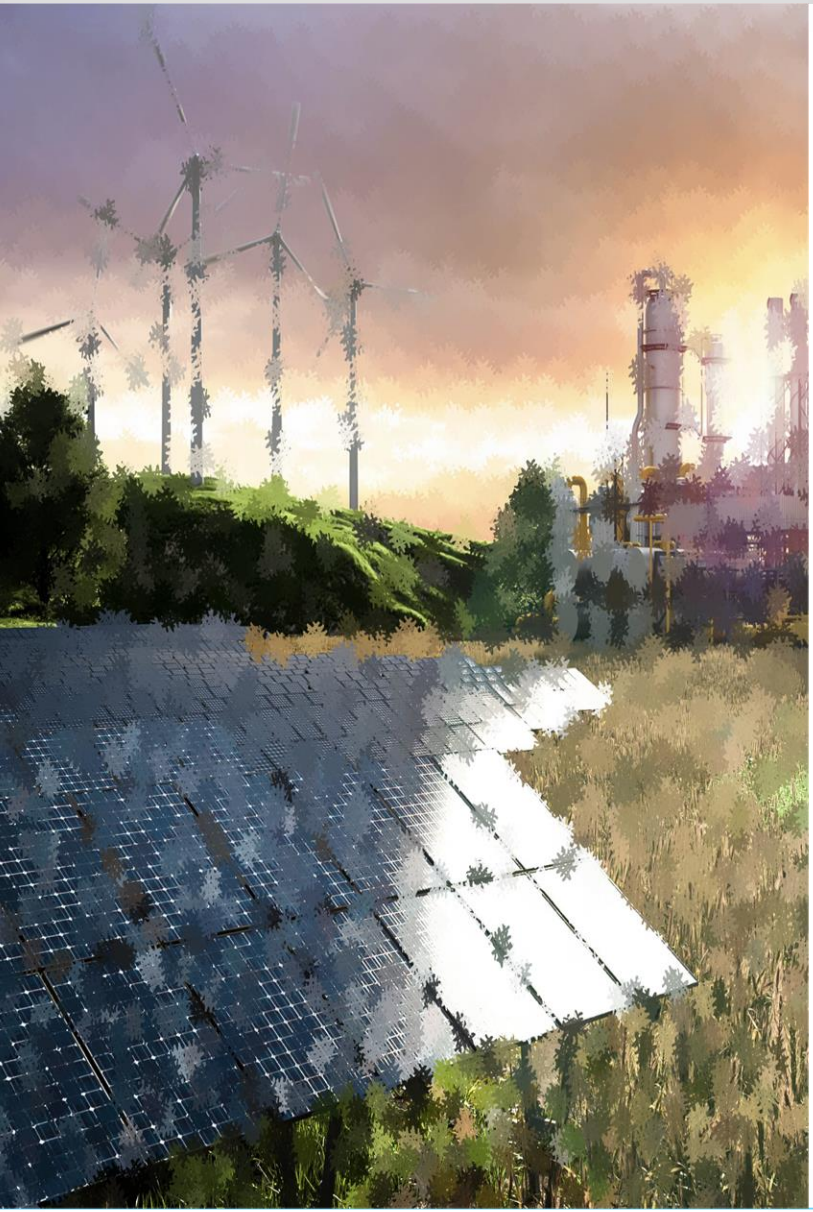

From sunlight and desert sand to a sustainable society

Thermochemical hydrogen storage: Redox reactor

Energy storage as metal ammine complexes

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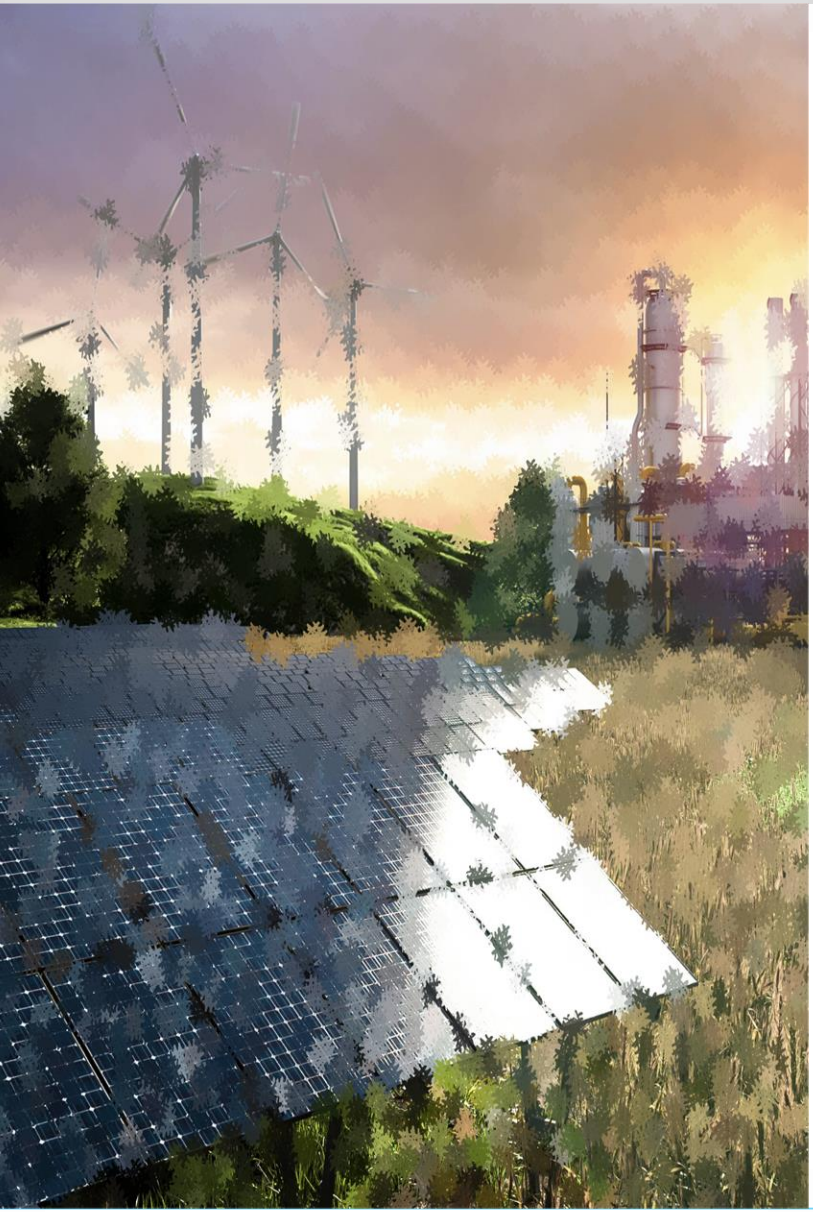
Acknowledgments



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