





"Techno-economic assessment of seasonal heat storage in district heating with thermochemical materials"

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System Boundary Definition



ting grid		(IVIVV)	(GWh)	(h)
A: ge urban"	peak	70	28	400
	base	20	100	5.000
B: all urban"	peak	20	7	350
	base	6	30	5.000
C: al"	peak	3	9	3.000
	base	1	5	5.000

grid "rui heat

demanc

full load

hours



Thermochemical Storage Materials Key parameters

- Three basic material groups investigated
 - Redox materials
 - Hydrates & Hydroxides
 - Zeolites
- Criteria for material selection
 - Reaction enthalpy (energy density) > 0.60 MJ/kg
 - Specific material costs < 0.10 €/MJ</p>
 - Availability > 200 t per month
 - Hazard categories allowing usage as storage material
 - Discharge reaction uses **oxygen** (air) or **water** (steam or moist air)
 - \rightarrow only one reactant has to be stored



Thermochemical Storage Materials Selected materials

	reactant	product	energy density (MJ/kg)	material price ¹⁾ (€/MJ)	availability (+ / ~ / -)	safety / hazard
zeolite	4A		0.65	0.484	+	classified as non-hazardous
	13X		0.86	0.834	+	classified as non-hazardous
hydrates & hydroxides	MgCl ₂	MgCl ₂ *6H ₂ O	4.24	0.0482)	+	GHS07; irritant
	MgCl ₂ 2H ₂ O	MgCl ₂ *6H ₂ O	1.92	0.076 ²⁾	+	GHS07; irritant
	MgSO ₄	MgSO ₄ *7H ₂ O	3.61	0.0232)	+	classified as non-hazardous
	MgSO ₄ H ₂ O	MgSO ₄ *7H ₂ O	2.37	0.0302)	+	classified as non-hazardous
	$AI_2(SO_4)_3$	Al ₂ (SO ₄) ₃ *6H ₂ O	1.79	0.084	+	GHS05; caustic
	CaO	Ca(OH) ₂	1.86	0.0802)	+	GHS05, GHS07; caustic, irritant
	MgO	Mg(OH) ₂	1.98	0.188	+	classified as non-hazardous
redox materials	Mg	MgO	24.75	0.025 ²⁾	+	GHS02; highly flammable
	Si	SiO ₂	32.43	0.097	~	GHS02, GHS07; highly flammable, irritant
	AI	AI_2O_3	31.05	0.072	+	GHS02; highly flammable
	Са	CaO	15.84	0.063	~	GHS02; highly flammable
	AIO	AI_2O_3	21.52	0.039	+	classified as non-hazardous
-						

¹⁾ source: search on B2B platforms, e.g., Alibaba

²⁾ Prices determined for product and mass converted to educt.

availability:



Thermochemical Storage Materials Restricting material properties

- Phase change of reactants during (dis)charge process, like liquefaction of MgSO₄
 → difficult to handle in certain reactor concepts
- Formation of hazardous substances (toxic/caustic), like gaseous HCl from MgCl₂ at high temperatures
- Risk of dust explosion since TCS materials require large specific surface area for optimum use
- **Passivation** through uncontrolled oxidation or humidification when stored at ambient conditions
- Feasibility of purely thermal reduction due to required temperature levels





Storage operations Charging the TCS

Energy Sources

- Solar heat
- Geothermal energy
- Industrial waste heat
- Electricity from renewables

Processes and Reactors

- **Drying** (zeolites, hydrates/hydroxides): circulation dryers, belt/roller dryers, <u>fluidized bed reactors</u>, <u>rotary kilns</u>, ...
- **Reduction** (redox materials): <u>electric arc furnace</u>, electrolysis, blast furnace, smelting reduction furnace, ...





Storage operations Discharging the TCS

Processes and Reactors

- Humidification (zeolites, hydrates/hydroxides):
 - Use of moist air was refused due to the high throughput required
 - Water vapour is preferred over liquid water to avoid decrease of net energy gained by heat of evaporation



• Reduction (redox materials): materials are expected to be conventionally combusted by using air or oxygen

Both processes are presumed to be feasible in **well-established reactor concepts**, like fluidized bed reactors, dust firing or grate reactors



Storage operations Transportation & Storage

- Required if charging and discharging
 reactors are spatially separated
- Safety classification of the material may increase transportation efforts and costs
- Usable transportation methods depend on location and transport connection of the reactor site



- According their properties and reactivity materials must be contained and not be exposed to environment
- Storage in **closed silos** was found to be a suitable method both on function and costs
- Closed depots were considered as an alternative in evaluations







Investigated Scenarios Humidification

<u>Scenario H1:</u>

- Charging and discharging in the same fluidized bed reactor
- Charging with solar thermal energy, discharging with steam not available for free
- Transportation by truck (100 km total) and storage in silos

Scenario H2:

- Charging and discharging in the **same** fluidized bed **reactor**
- Charging with industrial waste heat, discharging with steam available free of charge
- No transport and storage in closed depots

Scenario H3:

- Charging and discharging separate fluidized bed reactors
- Charging with deep geothermal energy, discharging with steam not available for free
- Transportation by rail freight (400 km total) and storage in closed depots





Investigated Scenarios Oxidation

Scenario O1:

- Charging by electric arc furnace, discharging in fluidized bed reactor
- Electricity from renewable energy sources
- Transportation by truck (100 km total) and storage in silos

Scenario O2:

- Charging by electric arc furnace, discharging by dust firing
- Electricity from renewable energy sources
- No transportation and storage in **closed depots**



Benchmarks

Alternative storage technologies and conventional district heating

- Most common form of large-scale heat storage is the utilization of sensible heat with hot water with specific costs down to 35 €/m³ for pit storages
- Average working price for district heating in Austrian provincial capitals at approx. 55 €/MWh was applied as first guideline due to grid specific conditions and high bandwidth of generation costs







Economic evaluation of the scenarios Results – Humidification



Scenario H1





Scenario H3

Economic evaluation of the scenarios Results – Humidification

Scenario H2





Economic evaluation of the scenarios Results – Humidification

Comparison to zeolites and other hydrates







Economic evaluation of the scenarios Results – Oxidation

Scenario O1



Scenario O2



Economic evaluation of the scenarios Results – Oxidation

 Ecological reasonability for redox materials is highly dependent on the use of low emission reduction procresses

TCS material	CO ₂ equivalent ¹	spec. CO ₂ emissions ¹					
	[kg _{CO2} /kg _{educt}]	[kg _{CO2} /GJ]					
RedOx AI - Al ₂ O ₃	3,82	123.02	Hall-Héroult process				
RedOx Ca - CaO	1,71	108.24	Aluminum from Hall-Héroult				
RedOx Si - SiO ₂	3,13	96.63	acc. to gross reaction				
RedOx Mg - MgO	1,81	73.16	Silicium acc. to gross reaction				
minimal CO ₂ emissions from reduction; does not include emissions from required energy (electricity), transportation, etc.							
Comparison to fossil fuels							
brown coal		110.9					
natural gas		55.9					

¹ calculations for stoichiometric reactions





Conclusions

- Choice of the heating grid has major influence on the potential use cases for TCS
 → grids with low power demand and high number of full load hours to be preferred
- Location of charging energy sources and distance to the heating grid should be kept low to save reactor and transportation costs
 - hydration-based materials show lowest costs when processed near industry
 - redox are preferable for long distances due to low transportation efforts
- Operating materials for reduction processes have not been considered and are expected to increase costs
- Use of inorganic salts (Bischofite, ...) instead of pure/synthetic materials could significantly decrease costs despite lower conversion efficiency and performance
- Zeolites are not suitable for large-scale applications due to low storage densities and high material price
- Considering expectable conversion rates, it will be hard for TCS to compete with hot water storages in larger grids. Therefore, future research should focus on optimization of materials, conversion technologies and storages for specific applications.







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