



Energy research Centre of the Netherlands

TCM materials for heat storage

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Inventory of TCM materials

First selection: Visscher 2004

- Hydrates, hydroxides (H₂O exchange)
- Carbonates (CO₂ exchange)
- Type of salt: chlorides and sulfates

A <=>	B +	C	GJ/m ³	T(°C)
MgSO ₄ · 7H ₂ O	MgSO ₄	7H ₂ O	2.8	122
SiO ₂	Si	O ₂	37.9	4065
FeCO ₃	FeO (wustite)	CO ₂	2.6	180
Fe(OH) ₂	FeO	H ₂ O	2.2	150
CaSO ₄ · 2H ₂ O	CaSO ₄	2H ₂ O	1.4	89
MgSO ₄ · H ₂ O	MgSO ₄	H ₂ O	1.3	216
ZnCO ₃	ZnO	CO ₂	2.5	133
CaCl ₂ · 2H ₂ O	CaCl ₂ · 1H ₂ O	H ₂ O	0.6	174
MgSO ₄ · 7H ₂ O	MgSO ₄ · 1H ₂ O	H ₂ O	2.3	105

Selection Criteria:

- Energy density
- Average Equilibrium Temperature
- Toxicity
- Abundance
- Pressure
- Corrosivity

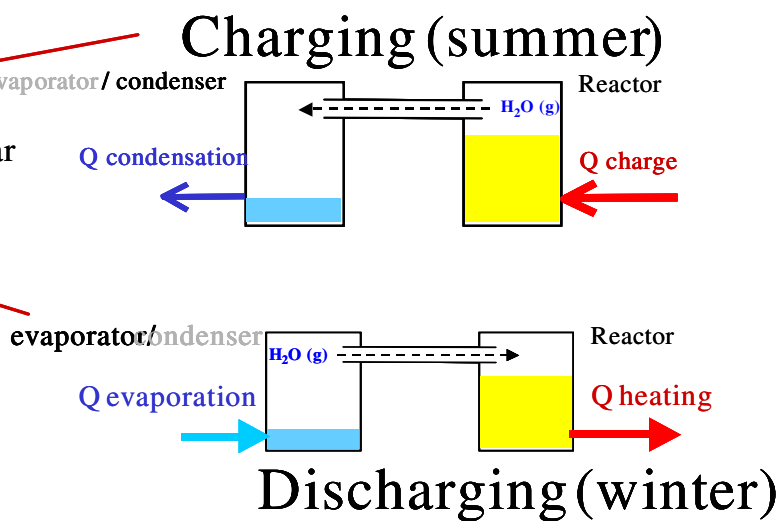
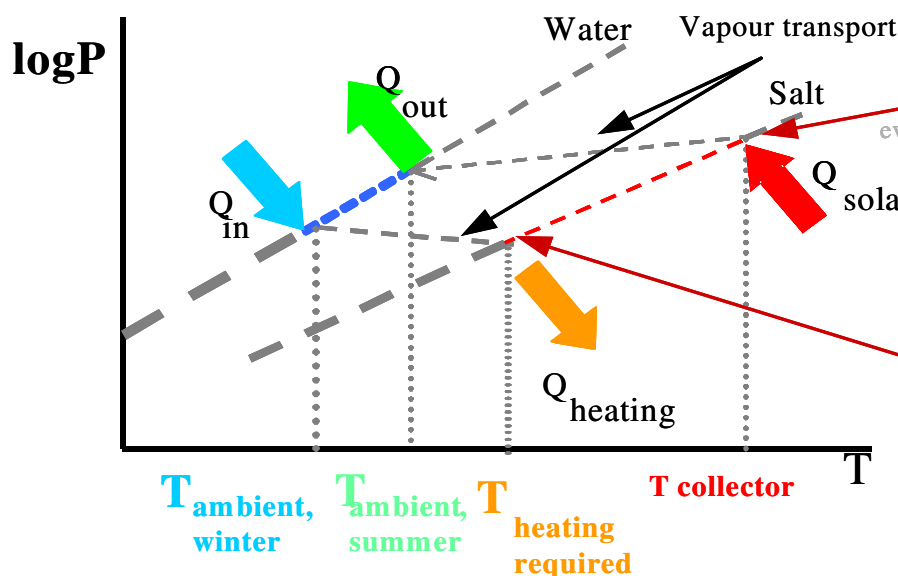
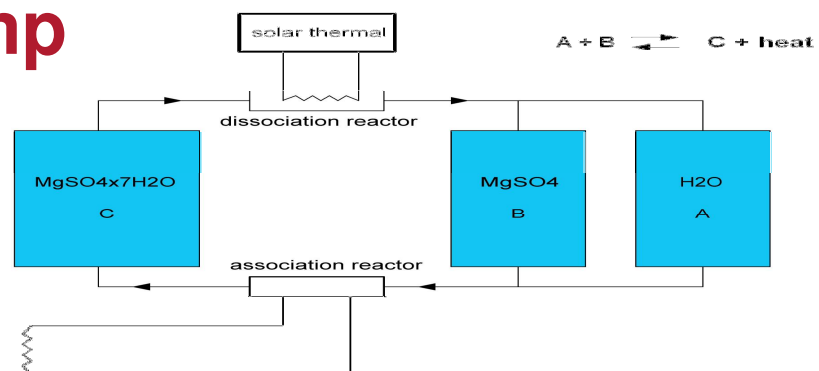
Inventory of TCM materials

New inventory:

- more detailed analysis of temperature level of different hydration steps
- More materials
 - Other sorption gasses (e.g. ammonia, methanol, hydrogen, etc)
 - More salts (bromides, carbonates, borates, nitrates, sulfides, oxides, etc.)

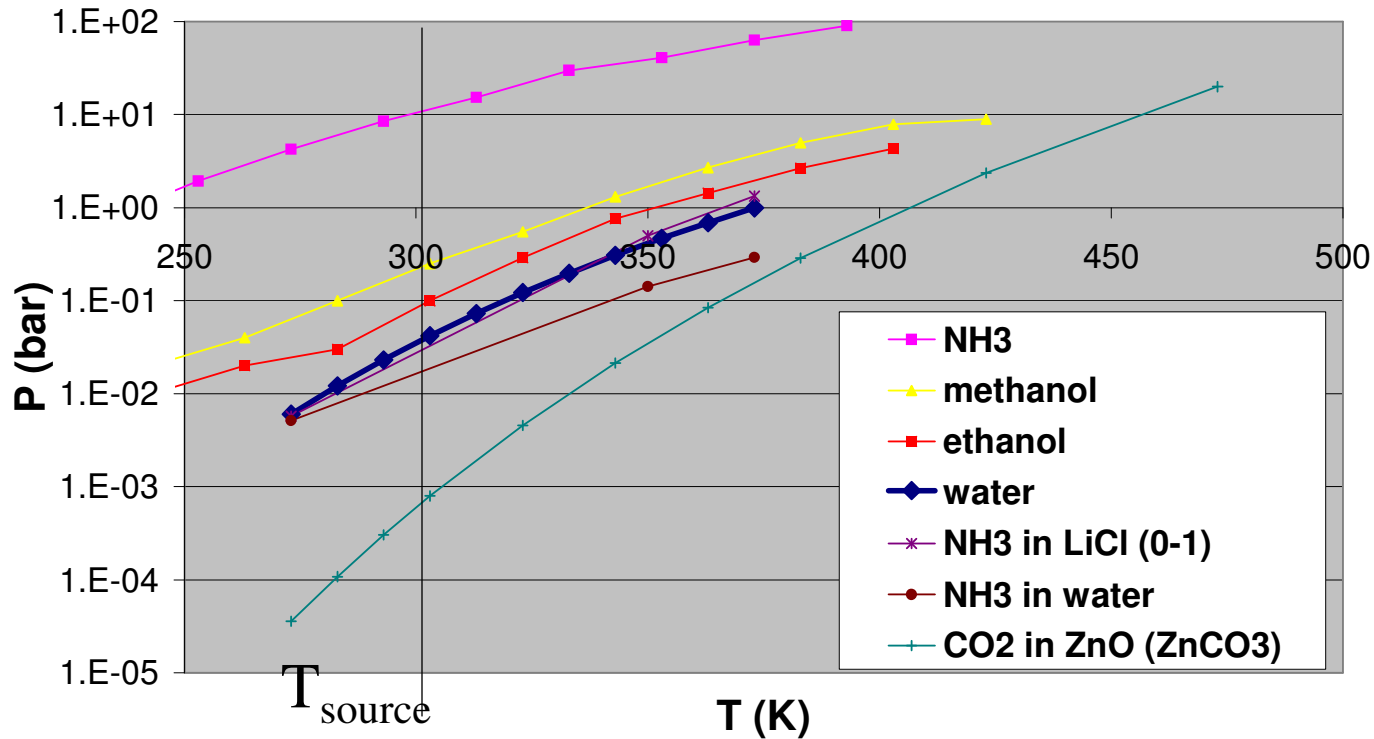
Absorption heat pump

For condensate or
adhesion to storage salt



Effect of sorption gas

P-T curves for various sorption vapours



High pressure: safety problem & large DT

Low pressure: power problem

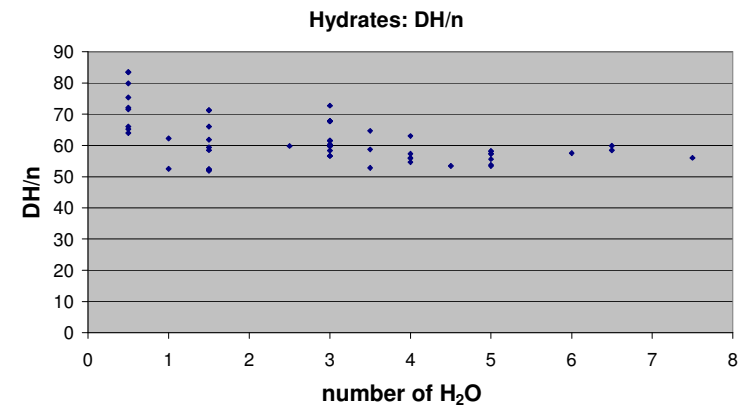
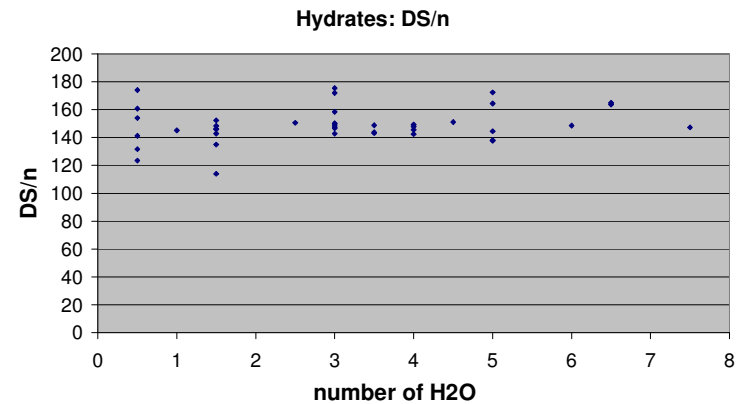
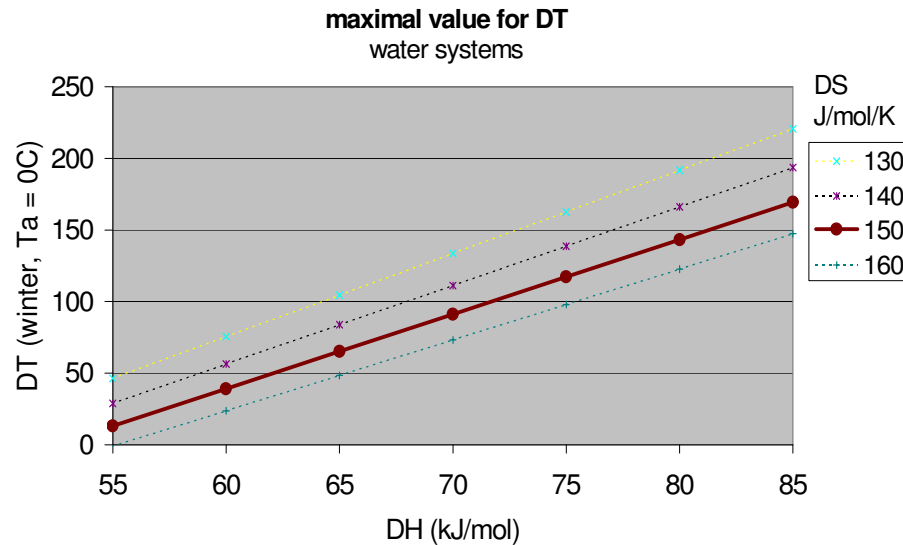
Hydrate salts

hydrates NBS																
	F	Cl	Br	I	O	S	Se	SeO4	OH	SO4	NO3	B4O7	PO4	ClO4	SiO3	CO3
Li	0	3	2	3	0	0	9	1	1	1	3	0	0	3	0	0
Na	0	0	2	2	0	9	16	10	7	10	0	10	10	1	9	10
K	2	0	0	0	0	5	19	0	2	0	0	0	0	0	0	1.5
Rb	1.5	0	0	0	0	0	0	0	2	0	0	0	0	0	0	3
Be	0	4	0	0	0	0	0	4	0.75	4	0	0	0	0	0	0
Mg	0	6	6	0	0	0	0	6	0	7	6	0	0	6	0	5
Ca	0	6	6	8	0	0	0	2	0	2	4	0	0	4	0	0
Sr	0	6	6	6	0	0	0	0	8	0	4	0	0	4	0	0
Ba	0	2	2	7	0	0	0	0	8	0	0	0	0	3	0	0
Al	0	6	0	0	3	0	0	0	0	18	9	0	0	0	2	0
Fe	0	6	0	0	0	0	0	0	0	7	9	0	2	6	0	0
Co	0	6	6	0	0	0	0	0	0	7	6	0	0	6	0	0
Ni	4	6	3	0	0	0	0	0	0	7	6	0	0	6	0	0
Cu	2	2	4	0	0	0	0	5	0	5	6	0	0	6	0	0
Zn	0	0	0	0	0	0	0	6	0	7	6	0	0	6	0	1
Na Al	3.5	0	0	0	0	0	0	0	0	12	0	0	0	0	1	0
K Al	3.5	0	0	0	0	0	0	12	0	12	0	0	0	0	0	0

Hydrate Salts - DH

DH: 80-55 kJ/mol

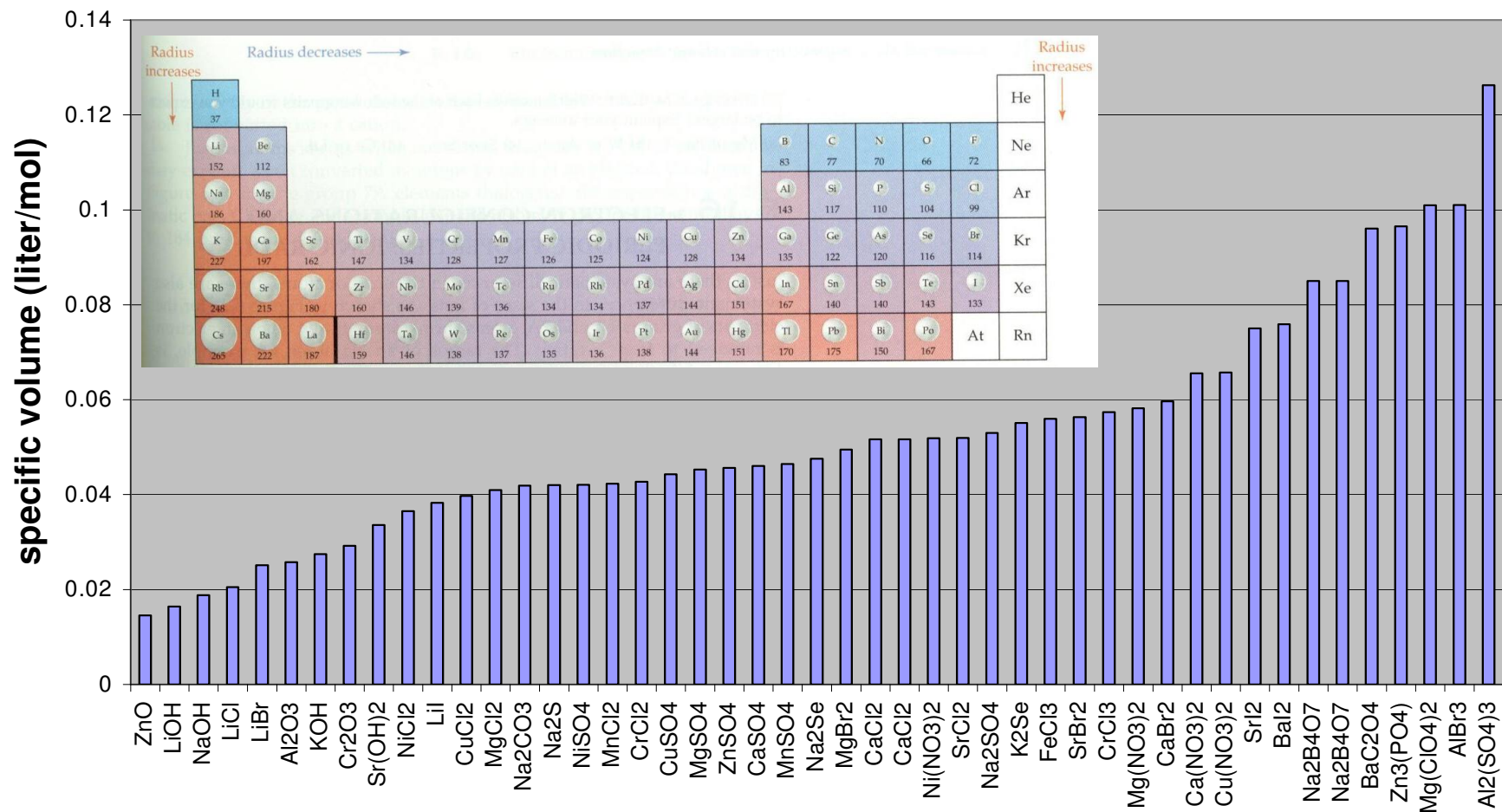
DS: ~150 J/mol/K



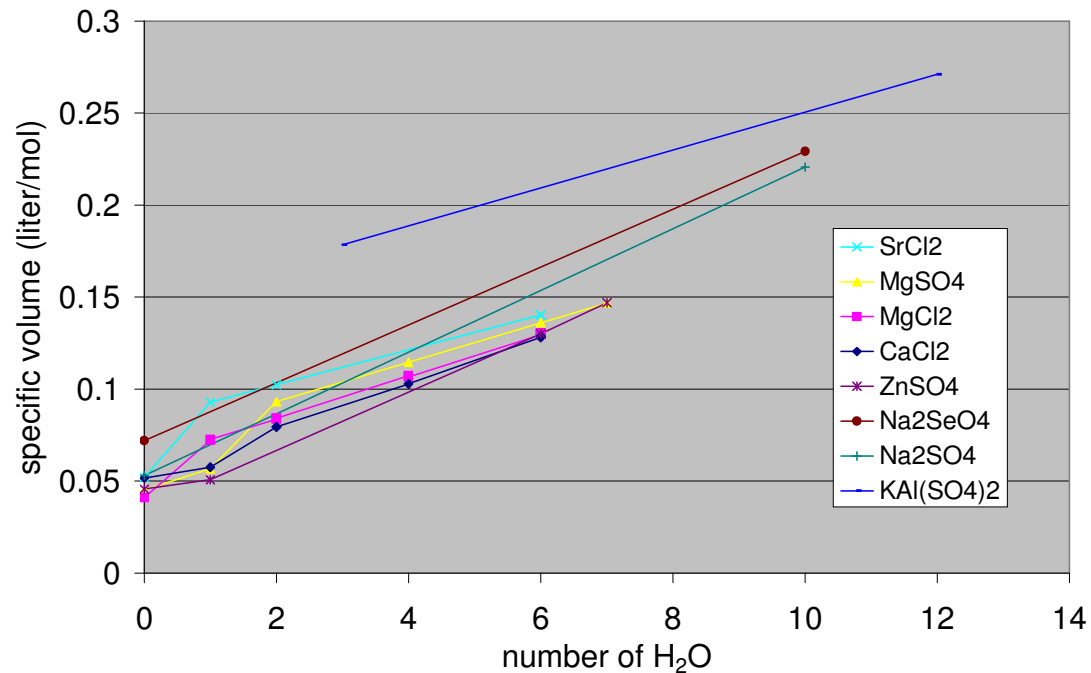
High DH: regeneration problem

Low DH: insufficient temperature step for use

Hydrate salts - volume



Hydrate salts - volume



Significant expansion due to hydration

- decrease of energy density
- risk for crystal integrity

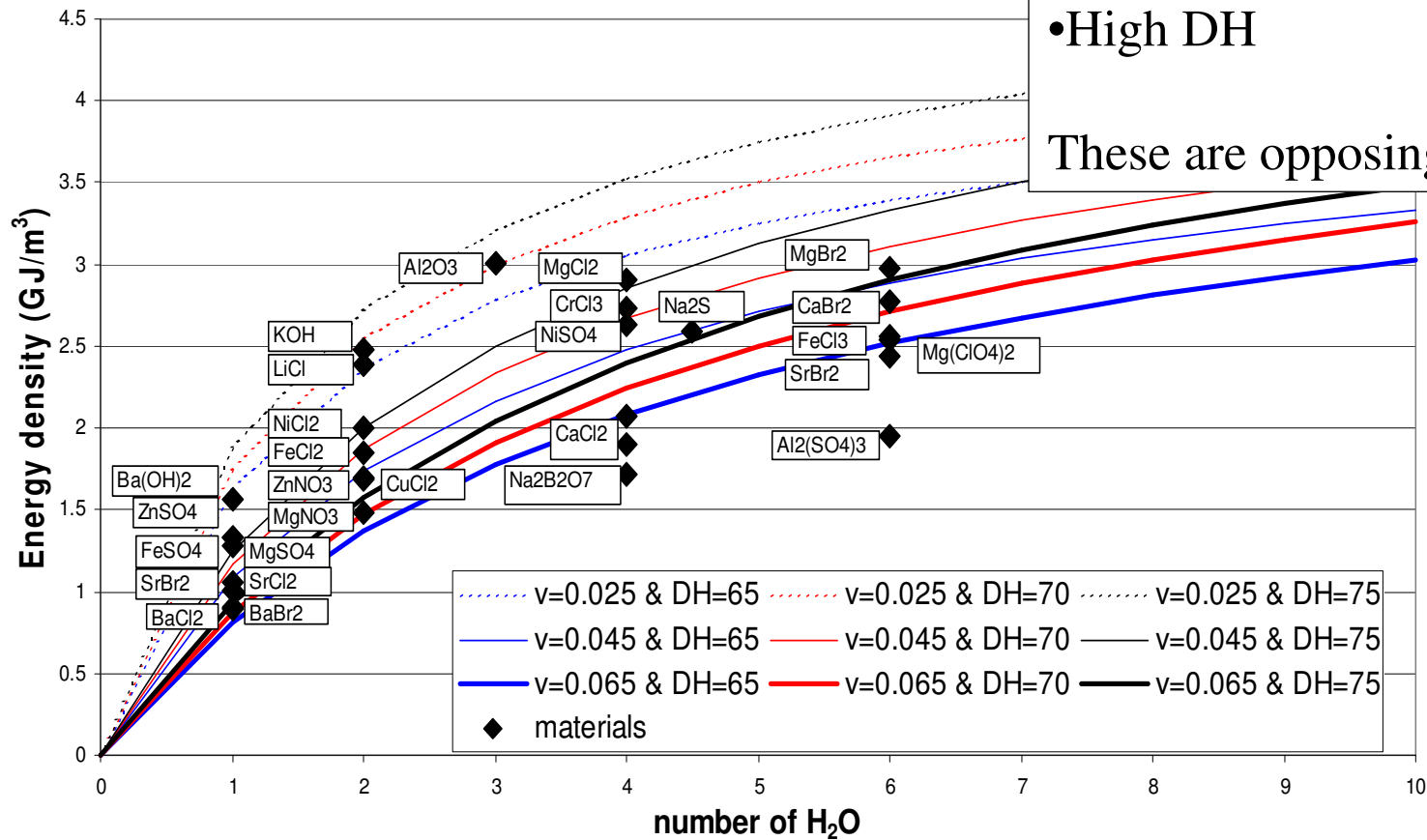
Hydrate salts - selection

Energy density

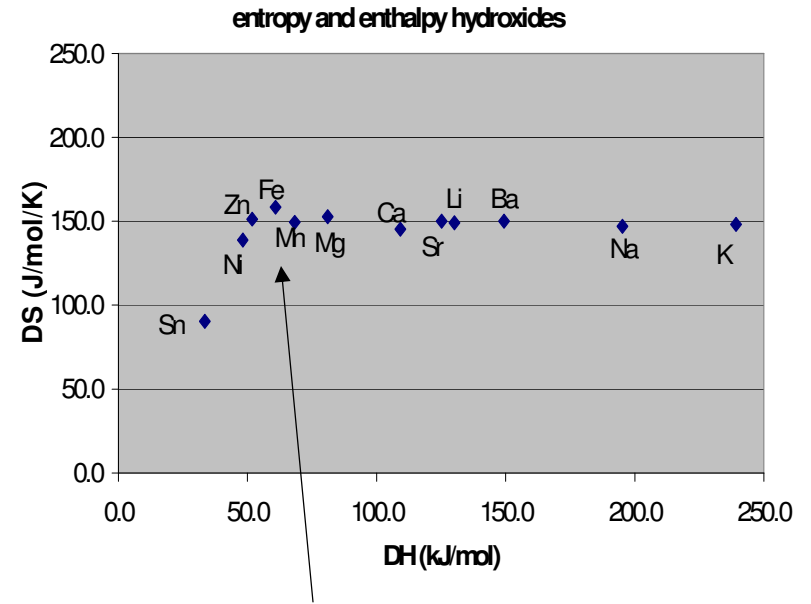
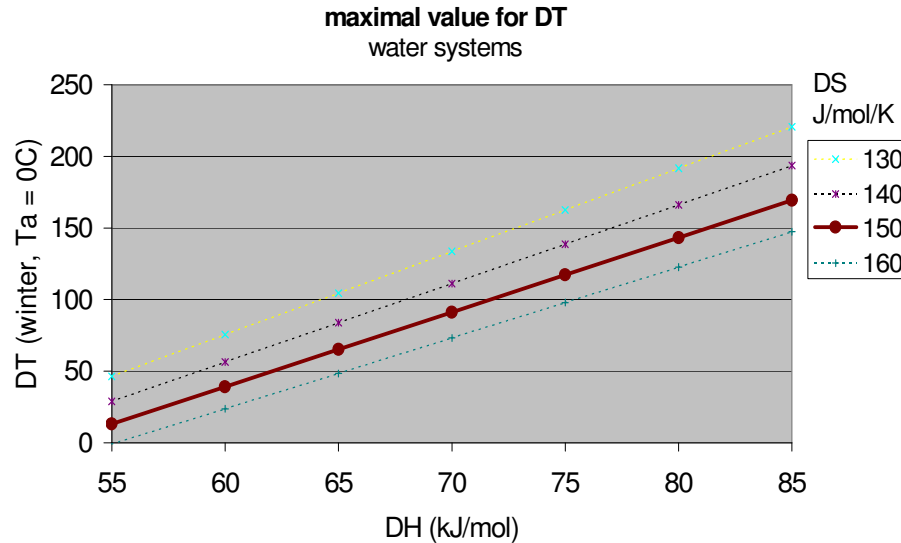
Good energy density:

- Small molecules
- Many H₂O
- High DH

These are opposing criteria!



Hydroxides



Correct range:

$\text{Fe}(\text{OH})_2$ 61 kJ/mol

$\text{Mn}(\text{OH})_2$ 68 kJ/mol

$\text{Mg}(\text{OH})_2$ 81 kJ/mol

High DH: regeneration problem

Low DH: insufficient temperature step for use

Selected materials

(list not yet finalised)

	Energy density (GJ/m ³)	Dhmax (kJ/mol)	Dhmin (kJ/mol)	abundance (ppm)	price (for analysis) euro/kg	toxicity (LD in mg/kg)	corrosivity	totaalscore
main list								
1 MgO->Mg(OH) ₂	3.2	81.0	81.0	23000.0	280.0	8500.0	1.0	8.8
3 Al ₂ (SO ₄) ₃ ->Al ₂ (SO ₄) ₃ x6H ₂ O	1.9	70.0	70.0	260.0	weinig?	>5000	1.0	8.1
2 MgCl ₂ ->MgCl ₂ x4H ₂ O	2.9	83.5	67.8	130.0	30.0	8100.0	5.0	7.8
4 ZnSO ₄ ->ZnSO ₄ x1H ₂ O	1.3	79.9	79.9	80.0	22.0	2949.0	1.0	7.6
5 MgSO ₄ x1H ₂ O	1.3	75.4	75.4	260.0	24.4	1200.0	1.0	6.9
6 LiBr	1.7	69.6	69.6	2.5	98.5	1800.0	?laag	7.1
7 Al ₂ O ₃ ->Al ₂ O ₃ x3H ₂ O	3.0	63.2	61.2	84100.0	25.8	5000.0	?niet	6.8
8 Mg(NO ₃) ₂ ->Mg(NO ₃) ₂ x2H ₂ O	1.5	67.5	67.5	20.0	46.0	5440.0	1.0	6.6
9 Zn(NO ₃) ₂ ->Zn(NO ₃) ₂ x2H ₂ O	1.7	79.5	63.5	80.0	69.5	1190.0	?niet	5.9
10 CaBr ₂ ->CaBr ₂ x6H ₂ O	2.8	62.1	62.1	2.5	63.0	2210.0	?niet	5.8
11 CaCl ₂ ->CaCl ₂ x4H ₂ O	1.9	71.6	61.5	130.0	15.9	1000.0	5.0	5.6
12 SrBr ₂ x1H ₂ O	1.0	72.0	72.0	2.5	172.0	1000.0	?niet	5.5
13 Na ₂ B ₄ O ₇ ->Na ₂ B ₄ O ₇ x4H ₂ O	1.7	62.3	62.3	10.0	96.5	2660.0	1.0	5.1
14 Ba(OH) ₂ ->Ba(OH) ₂ x1H ₂ O	1.6	62.0	62.0	250.0	62.0	550.0	1.0	3.8
15 Na ₂ S->Na ₂ Sx4.5H ₂ O	2.6	60.6	60.6	260.0	35.3	254.0	?sterk	3.7
possible extra options								
16 Mn(OH) ₂ ->MnO	2.5	68.4	68.4	1400.0	21.8	3475.0	1.0	8.3
17 KOH->KOHx2H ₂ O	2.5	82.3	60.3	1400.0	24.8	273.0	1.0	5.9
18 FeCl ₃ ->FeCl ₃ x6H ₂ O	2.6	62.2	62.2	130.0	66.5	900.0	5.0	4.4
19 FeCl ₂ ->FeCl ₂ x2H ₂ O	1.8	63.8	63.8	130.0	73.0	450.0	5.0	3.7
20 CuCl ₂ ->CuCl ₂ x2H ₂ O	1.7	58.8	58.8	75.0	79.5	584.0	1.0	3.0
eliminated due to toxicity etc								
MgClO ₄ ->MgClO ₄ x6H ₂ O	2.5	83.1	62.3	130.0	234.0	50.0	?hoog	5.4
NiCl ₂ ->NiCl ₂ x2H ₂ O	2.0	66.6	66.6	105	95	105	4	4.5
LiCl->LiClx2H ₂ O	2.4	62.2	58.3	13	171	526	1	3.9
NiSO ₄ ->NiSO ₄ x4H ₂ O	2.6	66.0	66.0	105	104	264	1	5.8
LiOH->LiOHx1H ₂ O	2.0	61.3	61.3	13.0	145.0	1.0	?laag	3.1