

**Deliverable D3.1: A ranking of salt hydrates
with hydration / dehydration reactions
within the temperature range (90-150°C
and 148-253°C)**



**Funded by
the European Union**

This project has received funding from European Union's Horizon Europe's Research and Innovation Program under grant agreement No. 101103966. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Climate, Infrastructure and Environment Executive Agency (CINEA). Neither the European Union nor the granting authority can be held responsible for them.

Deliverable 3.1

Actual Submission Date: **29/02/2024**

Produced by: **TUW: Jakob Smith, Frieda Kapsamer, Peter Weinberger**

TechUPGRADE

techupgrade.eu

HORIZON-CL5-2022-D4-01

Thermochemical Heat Recovery and Upgrade for Industrial Processes

Grant Agreement no.: 101103966

Start date of project: 1 May 2023 - Duration: 48 months

DELIVERABLE FACTSHEET

Deliverable D3.1	
Nature of the Deliverable:	D3.1: A ranking of salt hydrates...
Due date of the Deliverable:	M12 – 29/02-2024
Actual Submission Date:	M12 – 29/02-2024
Produced by:	JS: Jakob Smith
Contributors:	FK: Frieda Kapsamer
Work Package Leader	PW: Peter Weinberger
Reviewed by:	HRR: Hamid Reza Rahbari

Dissemination level	
X	PU = Public
	PP = Restricted to other programme participants (including the EC)
	RE = Restricted to a group of the consortium (including the EC)
	CO = Confidential, only members of the consortium (including the EC)

Contents

1	Public Summary.....	5
2	List of potential candidates with discussion	5
2.1	Reactions of interest for 90-150 °C	5
2.2	Reactions of interest for 148-253 °C	7
2.3	Reactions of interest with no equilibrium temperature given.....	8
3	Bibliography.....	10

Tables

Table 1. Reactions of interest for the equilibrium temperature range 90-150°C from the Vienna TCES Database, ranked from most to least promising.	7
--	---

Table 2. Reactions of interest for the equilibrium temperature range 148-253°C from the Vienna TCES Database, ranked from most to least promising.	8
---	---

Table 3. Reactions of interest with no equilibrium data given from the Vienna TCES Database, ranked from most to least promising.....	9
---	---

1 Public Summary

In order to identify suitable thermochemical energy storage materials, the Vienna TCES Database was consulted [1]. This database was constructed using a systematic search algorithm to identify reactions involving the separation of an inorganic solid from a gas or vapor commonly used in industry. The HSC chemistry data base served as the source of thermodynamic data. Having selected water as the sole gaseous reaction partner, a list containing of reactions salt hydrates and a few hydroxides was generated. These reactions were sorted into those with an equilibrium temperature (as calculated with 1 bar of water vapor under standard conditions from the reaction enthalpies ΔH and reaction entropies taken from the HSC database) between 90-150°C and 148-253 °C, the lower temperature waste heat being available from an electrolyser at ca. 70°C and the higher temperature waste heat being available in a Rendo heat storage system that provides pressurized hot water at 140°C. Furthermore, the reactions of unknown equilibrium temperature were also considered.

After excluding candidates that seemed certain to fail to meet two critical requirements (cost $< \text{€}3/\text{kg}$ and energy density $> 300 \text{ kWh}/\text{m}^3$), a short list of reactions included both SrCl_2 and K_2CO_3 for both temperature ranges. Furthermore, Cs_2CO_3 , LaCl_3 , and ZnSO_4 may be of some interest at lower temperatures, whereas CaCl_2 , SmCl_3 , and BaI_2 may be of use at higher temperatures. Finally, interesting materials of database-unknown thermodynamic properties include CuHPO_4 , FePO_4 , and $\text{Cr}_2(\text{SO}_4)_3$.

2 List of potential candidates with discussion

2.1 Reactions of interest for 90-150 °C

In order to select the most promising candidates for further experimental investigation, readily available data such as toxicological properties, cost, and thermodynamic data were considered. In the few cases where cycle stability has already been determined for different applications, these results need to be verified for the present application. Among the most promising candidates in the database is entry 1 of Table 1, strontium bromide. The related strontium chloride is also worthy of mention, being notably cheaper and thus better corresponding to the cost requirements for the final material. Potassium carbonate would be advantageous due to the non-toxic and abundant nature of its constituent elements. Entry 5, Lanthanum (III) chloride, is one of the less widely researched literature-known TCES candidates, perhaps due to its rather high material cost. Some studies indicate that the compound is cycle-stable, but a significant dehydration occurs even before 90°C, making the candidate of only limited usefulness for the present applications [2-3].

Zinc sulphate appears to be a suitable candidate at first glance; however, work by Rehman *et al.* indicates that this material suffers a decrease of its reaction enthalpy within 100 cycles [4]. As their work did not attempt to elucidate the reasons for the decrease in enthalpy or ameliorate it, the material may still conceivably be salvageable through chemical modification, choice of particle size, or other methods. The cement phases of entry 7 are likely difficult to synthesize in pure form. Entry 8, like many alums, suffers from a low melting point, and the danger of ammonia escaping from the compound is also undesirable.

Entry 9, sodium pyrophosphate, again exhibits favorable toxicological and economic properties, but the low melting point of the decahydrate (80°C) is not ideal for the application. The calcium borate of entry 10 suffers from the disadvantage of requiring mechanical

activation for use at low temperatures [5]. The nitrates of copper and zinc, entries 11 and 15, contain the unfavorable nitrate ion, which may be released at high temperatures, oxidize, explode upon heating, or generate nitric acid. Finally, the selenite and tellurite compounds, entries 13 and 14, are of little interest due to the expensive and toxic nature of the anions present.

Table 1. Reactions of interest for the equilibrium temperature range 90-150°C from the Vienna TCES Database, ranked from most to least promising.

	Reaction	T eq (°C)	ΔH eq (kJ/mol)
1	SrBr ₂ *6H ₂ O --> 5 H ₂ O + SrBr ₂ *H ₂ O	128,4	284
	SrBr ₂ *6H ₂ O --> 6 H ₂ O + SrBr ₂	144,3	354
2	SrCl ₂ *6H ₂ O --> 4 H ₂ O + SrCl ₂ *2H ₂ O	97,8	240
	SrCl ₂ *6H ₂ O --> 5 H ₂ O + SrCl ₂ *H ₂ O	129,6	308
	SrCl ₂ *6H ₂ O --> 6 H ₂ O + SrCl ₂	118,1	365
3	2 K ₂ CO ₃ *1.5H ₂ O --> 3 H ₂ O + 2 K ₂ CO ₃	148,3	200
4	2 Cs ₂ CO ₃ *3.5H ₂ O --> 7 H ₂ O + 2 Cs ₂ CO ₃	145,8	451
5	LaCl ₃ *7H ₂ O --> 7 H ₂ O + LaCl ₃	145,0	403
6	ZnSO ₄ *6H ₂ O --> 6 H ₂ O + ZnSO ₄	119,5	344
	ZnSO ₄ *7H ₂ O --> 6 H ₂ O + ZnSO ₄ *H ₂ O	93,5	324
	ZnSO ₄ *7H ₂ O --> 7 H ₂ O + ZnSO ₄	115,9	403
7	2(CaO) ₅ (SiO ₂) ₆ *5.5H ₂ O --> 5 H ₂ O + 2(CaO) ₅ (SiO ₂) ₆ *3H ₂ O	119,3	290
	(CaO) ₅ (SiO ₂) ₆ *10.5H ₂ O --> 5 H ₂ O + (CaO) ₅ (SiO ₂) ₆ *5.5H ₂ O	106,8	281
	2(CaO) ₅ (SiO ₂) ₆ *10.5H ₂ O --> 15 H ₂ O + 2(CaO) ₅ (SiO ₂) ₆ *3H ₂ O	111,0	851
8	NH ₄ *Al(SO ₄) ₂ *12H ₂ O --> 12 H ₂ O + NH ₄ *Al(SO ₄) ₂	112,9	678
9	Na ₄ P ₂ O ₇ *10H ₂ O --> 10 H ₂ O + Na ₄ P ₂ O ₇	95,1	535
10	2 CaB ₃ O ₄ (OH) ₃ *H ₂ O --> 5 H ₂ O + *2CaO*3B ₂ O ₃	109,3	350
11	Cu(NO ₃) ₂ *6H ₂ O --> 6 H ₂ O + Cu(NO ₃) ₂	114,1	373
12	NdCl ₃ *6H ₂ O --> 6 H ₂ O + NdCl ₃	135,5	360
13	MgSeO ₃ *6H ₂ O --> 6 H ₂ O + MgSeO ₃	107,7	376
14	MgTeO ₃ *5H ₂ O --> 5 H ₂ O + MgTeO ₃	105,3	318
	MgTeO ₃ *6H ₂ O --> 6 H ₂ O + MgTeO ₃	100,2	372
15	Zn(NO ₃) ₂ *6H ₂ O --> 6 H ₂ O + Zn(NO ₃) ₂	104,7	387

2.2 Reactions of interest for 148-253 °C

The previously discussed strontium and potassium compounds are once again forerunners for the temperature range at hand (entries 1-3 of Table 2). Although calcium chloride, entry 4, has like many other chlorides often been considered for use in thermochemical energy storage, the potential problematic evolution of hydrogen chloride at higher temperatures must be taken into account. Nonetheless, calcium chloride would be a very desirable material due to its benign environmental impact and low cost. As it is readily available, no synthesis is needed.

Entry 5, samarium (III) chloride, is rather expensive and is worthy of mention primarily due to its novelty. The salt is slightly toxic, causing skin irritation. Barium iodide, entry 6, is rather expensive due to its anion, and the compound is highly soluble in water. The calcium aluminate, entry 7, may require undesirably high reaction temperatures and is likely difficult to synthesize. However, due to the inexpensive and readily available elements contained in the compound, its large-

scale synthesis may nonetheless be economically feasible. Entry 8, magnesium chloride, can also suffer from hydrogen chloride evolution at higher temperatures, but lower temperature applications may still be possible. Finally, magnesium sulphate exhibits poor hydration kinetics, thus requiring significant efforts to improve its suitability. Due to their benign toxicological profile and low cost, these magnesium salts would be ideal candidates if all other problems can be overcome.

Table 2. Reactions of interest for the equilibrium temperature range 148-253°C from the Vienna TCES Database, ranked from most to least promising.

	Reaction	T eq (°C)	ΔH eq (kJ/mol)
1	$\text{SrBr}_2 \cdot \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{SrBr}_2$	207,6	137
2	$\text{SrCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{SrCl}_2 \cdot \text{H}_2\text{O}$	188,6	413
	$\text{SrCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow 2 \text{H}_2\text{O} + \text{SrCl}_2$	167,5	146
3	$2 \text{K}_2\text{CO}_3 \cdot 0.5\text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + 2 \text{K}_2\text{CO}_3$	171,1	366
	$2 \text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O} \rightarrow 3 \text{H}_2\text{O} + 2 \text{K}_2\text{CO}_3$	148,3	78
4	$\text{CaCl}_2 \cdot \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{CaCl}_2$	206,7	407
5	$\text{SmCl}_3 \cdot 6\text{H}_2\text{O} \rightarrow 6 \text{H}_2\text{O} + \text{SmCl}_3$	161,6	393
6	$\text{BaI}_2 \cdot 2\text{H}_2\text{O} \rightarrow 2 \text{H}_2\text{O} + \text{BaI}_2$	161,6	356
7	$*3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} \rightarrow 6 \text{H}_2\text{O} + *3\text{CaO} \cdot \text{Al}_2\text{O}_3$	221,6	363
8	$\text{MgCl}_2 \cdot 4\text{H}_2\text{O} \rightarrow 2 \text{H}_2\text{O} + \text{MgCl}_2 \cdot 2\text{H}_2\text{O}$	191,3	401
	$\text{MgCl}_2 \cdot 4\text{H}_2\text{O} \rightarrow 3 \text{H}_2\text{O} + \text{MgCl}_2 \cdot \text{H}_2\text{O}$	200,0	317
	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow 4 \text{H}_2\text{O} + \text{MgCl}_2 \cdot 2\text{H}_2\text{O}$	171,1	360
	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow 6 \text{H}_2\text{O} + \text{MgCl}_2$	200,9	386
9	$\text{MgSO}_4 \cdot 4\text{H}_2\text{O} \rightarrow 4 \text{H}_2\text{O} + \text{MgSO}_4$	175,5	327
	$\text{MgSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow 5 \text{H}_2\text{O} + \text{MgSO}_4$	160,4	468

2.3 Reactions of interest with no equilibrium temperature given

Table 3 contains a series of interesting and underresearched compounds. Entry 1, copper (II) hydrogen phosphate, releases its crystal water at 145°C and suffers from only mild cost issues. Entry 2, iron (III) phosphate, dehydrates around 180°C; phosphates are often known to have slow kinetics, which may also be problematic in this case. However, the low cost and benign toxicological properties of iron and phosphates in general are advantageous. Entry 3, chromium (III) sulphate, is an interesting candidate, but the melting point of 90°C of a hydrated species is not ideal for the application. The human toxicity and ecotoxicity of this material are significant disadvantages.

Entry 4, rankinite, may require difficult synthetic conditions. However, if a suitable synthesis can be found, upscaling may be simple. The toxicologically benign elements are promising. Entry 7 suffers from the costs associated with molybdenum and a low energy storage density for the monohydrate. Entry 8, aluminum phosphate, has some similar properties to the isoelectronic silicon dioxide; thus, a broad dehydration interval may be expected. Although tin is rather expensive and the reversibility of entry 9 is questionable, the reaction is noteworthy due to its novelty.

Entry 10 is a salt of toxic formic acid, whereas entry 11 also includes a toxic anion. Entry 12, like entry 9, represents the decomposition of a hydroxide, which may not be reversible. The sulfates of entries 13 and 14 both suffer from toxicity issues but may still be useful. Finally, entry 15, cobalt selenite, is included for the sake of completeness despite toxicity and cost issues [6-7].

Table 3. Reactions of interest with no equilibrium data given from the Vienna TCES Database, ranked from most to least promising.

	Reaction
1	$2 \text{CuHPO}_4 \cdot \text{H}_2\text{O} \rightarrow 3 \text{H}_2\text{O} + \text{Cu}_2\text{P}_2\text{O}_7$
2	$\text{FePO}_4 \cdot 4\text{H}_2\text{O} \rightarrow 2 \text{H}_2\text{O} + \text{FePO}_4 \cdot 2\text{H}_2\text{O}$ $\text{FePO}_4 \cdot 4\text{H}_2\text{O} \rightarrow 4 \text{H}_2\text{O} + \text{FePO}_4$
3	$\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} \rightarrow 10 \text{H}_2\text{O} + \text{Cr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ $\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} \rightarrow 18 \text{H}_2\text{O} + \text{Cr}_2(\text{SO}_4)_3$ $\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} \rightarrow 4 \text{H}_2\text{O} + \text{Cr}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$
4	$3 \text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} \rightarrow 3 \text{H}_2\text{O} + \text{Ca}_3\text{Si}_2\text{O}_7$
5	$\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} \rightarrow 12 \text{H}_2\text{O} + \text{KCr}(\text{SO}_4)_2$
6	$\text{Ca}_2\text{Al}_4\text{Si}_{14}\text{O}_{36} \cdot 14\text{H}_2\text{O} \rightarrow 2 \text{H}_2\text{O} + 2 \text{CaAl}_2\text{Si}_7\text{O}_{18} \cdot 6\text{H}_2\text{O}$
7	$\text{Na}_2\text{MoO}_4 \cdot \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{Na}_2\text{MoO}_4$
8	$\text{AlPO}_4 \cdot 2\text{H}_2\text{O} \rightarrow 2 \text{H}_2\text{O} + \text{AlPO}_4$
9	$\text{Sn}(\text{OH})_4 \rightarrow 2 \text{H}_2\text{O} + \text{SnO}_2$
10	$\text{NaCHOO} \cdot 3\text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{NaCHOO} \cdot 2\text{H}_2\text{O}$
11	$\text{AlF}_3 \cdot 3\text{H}_2\text{O} \rightarrow 3 \text{H}_2\text{O} + \text{AlF}_3$
12	$2 \text{Cr}(\text{OH})_3 \rightarrow 3 \text{H}_2\text{O} + \text{Cr}_2\text{O}_3$
13	$\text{MnSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow 4 \text{H}_2\text{O} + \text{MnSO}_4 \cdot \text{H}_2\text{O}$ $\text{MnSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow 5 \text{H}_2\text{O} + \text{MnSO}_4$ $\text{MnSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{MnSO}_4 \cdot 4\text{H}_2\text{O}$
14	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O} \rightarrow 2 \text{H}_2\text{O} + \text{NiSO}_4 \cdot 4\text{H}_2\text{O}$ $\text{NiSO}_4 \cdot 6\text{H}_2\text{O} \rightarrow 5 \text{H}_2\text{O} + \text{NiSO}_4 \cdot \text{H}_2\text{O}$ $\text{NiSO}_4 \cdot 7\text{H}_2\text{O} \rightarrow 3 \text{H}_2\text{O} + \text{NiSO}_4 \cdot 4\text{H}_2\text{O}$
15	$\text{CoSeO}_3 \cdot 2\text{H}_2\text{O} \rightarrow 2 \text{H}_2\text{O} + \text{CoSeO}_3$

3 Bibliography

1. Deutsch, M., et al. (2016). "Systematic search algorithm for potential thermochemical energy storage systems." Applied Energy **183**: 113-120.
2. Okhrimenko, L., et al. (2022). "Thermodynamic equilibrium and kinetic study of lanthanum chloride heptahydrate dehydration for thermal energy storage." Journal of Energy Storage **48**.
3. Gong, Z., et al. (1983). "A Study of Dehydration Process of Lanthanum Chloride Heptahydrate." Acta Chimica Sinica **41**(5): 391-396.
4. Rehman, A. U., et al. (2020). "Hydration performance and cycling stability of three TCM: MgSO₄, ZnSO₄ and FeSO₄." International Journal of Energy Research **44**(8): 6981-6990.
5. Uysal, T., et al. (2016). "Effects of mechanical activation of colemanite (Ca₂B₆O₁₁•5H₂O) on its thermal transformations." International Journal of Mineral Processing **151**: 51-58.
6. Ebert, M., et al. (1982). "Cobalt(II) Selenites." Chemicke Zvesti **36**(2): 169-177.
7. Park, J. S., et al. (2021). "Exploration of cobalt selenite-carbon composite porous nanofibers as anode for sodium-ion batteries and unveiling their conversion reaction mechanism." Journal of Materials Science & Technology **89**: 24-35.



CONTACT US

techupgrade.eu

FOLLOW US



Funded by
the European Union

This project has received funding from European Union's Horizon Europe's Research and Innovation Program under grant agreement No. 101103966. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Climate, Infrastructure and Environment Executive Agency (CINEA). Neither the European Union nor the granting authority can be held responsible for them.