ASSESSMENT OF THERMODYNAMIC EQUILIBRIUM PROPERTIES OF SALT HYDRATES FOR HEAT TRANSFORMATION APPLICATIONS AT DIFFERENT TEMPERATURE LEVELS

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1 INTRODUCTION

The use of hydration reactions of hygroscopic salts for thermochemical applications like thermal storage and thermally driven cooling or heat pumping has attracted rising interest (Aristov 2013; N'Tsoukpoe et al. 2014; Solé et al. 2015). A similar field of application is for humidity control (Glasser 2014).

This theoretical work focusses on the question of the suitability of salt hydrate reactions for given temperature boundary conditions of any target application, i.e. temperatures of heat absorption and release of the different cycle phases. This adds an often neglected aspect to common evaluation criteria thermal storage density and cycle efficiency. The scope is solid-solid reactions with water as a working fluid. Hence, ammoniates or alcoholates are not considered neither reactions purposely including (partial) liquefaction of the salt hydrate. The latter may be the case for salt hydrates dispersed in porous media (Gordeeva, Aristov 2012) or in a stable host matrix (Hallström et al. 2014).

2 METHODS

2.1 Ideal cycle

The salt hydrates are assessed based on the ideal single stage single step closed sorption cycle shown in Figure 1. The hydration reaction

$$M_aX_b \cdot nH_2O(c) + \Delta nH_2O(g) \rightleftarrows M_aX_b \cdot mH_2O(c) \qquad [1]$$

occurs in a single step between the crystalline salt hydration levels m and n with $\Delta n = m - n$, where n can be zero. The inorganic salt M_aX_b consists of a cations and b anions. In the following the short form $M_aX_b \cdot (m-n)\mathrm{H_2O}$ will be used for Eq [1].

The equilibrium condition, i.e. saturation pressure $p_{s,sat}(T)$, of this reaction is shown as the dashed line in Figure 1. The melting point of the higher hydrate T_{mlt} is the stability boundary of Eq [1]. In the closed

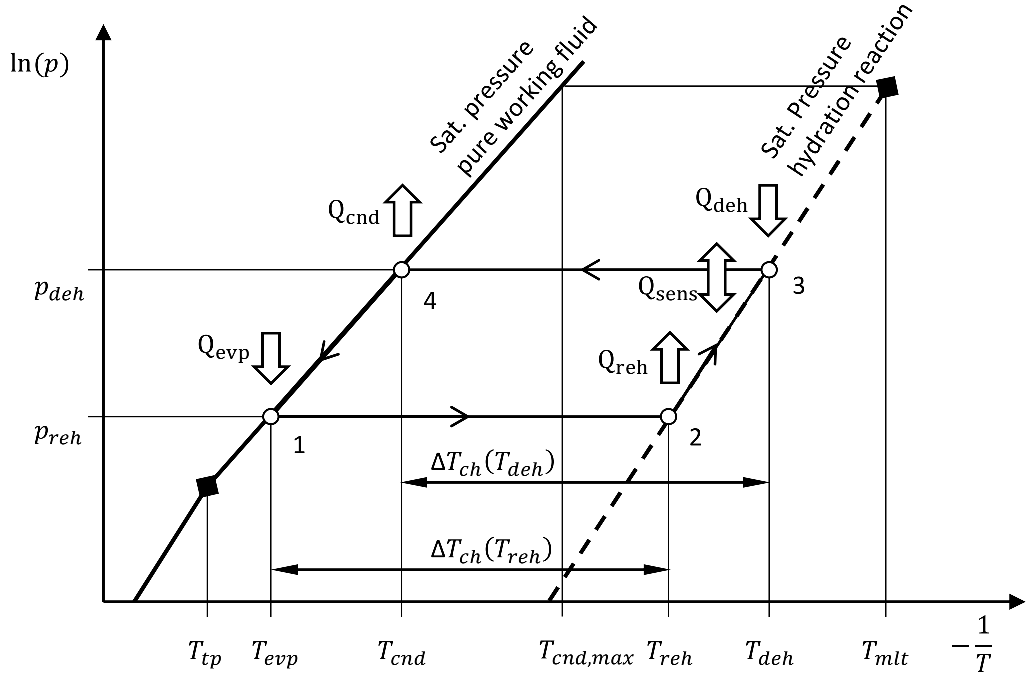

Figure 1: Clausius-clapeyron diagram of the ideal single step closed sorption cycle (1: evaporation, 2: rehydration, 3: dehydration, 4: condensation)

cycle the gaseous working fluid (water) is condensed and evaporated at its saturation pressure $p_{wf,sat}(T)$ (solid line). Below the triple point temperature T_{tp} the working fluid would be sublimed at the saturation pressure of pure ice.

The cycle proceeds as follows: At the rehydration pressure p_{reh} the working fluid is evaporated (1) at temperature T_{evp} absorbing the evaporation heat Q_{evp} and reacts with the salt (2) in a *single step* to the higher hydration level at the temperature T_{reh} releasing Q_{reh}. Once all salt is at the higher hydration level, the amount of heat $Q_{sens,wet}$ is applied in order to bring the "wet" salt hydrate to temperature T_{deh} and pressure p_{deh} where the dehydration (3) takes place when Q_{deh} is applied. At the same time the gaseous working fluid is condensed at temperature T_{cnd} releasing Q_{cnd} (4). After complete dehydration to the lower hydration level, the system is brought back to rehydration pressure by cooling (removing $Q_{sens,dry}$) the "dry" salt hydrate. The liquid working fluid is cooled down to T_{evp} by partial evaporation.

To avoid (partial) melting of the material the condensation temperature may not exceed $T_{cnd,max}$.

2.2 Equilibrium properties and sorption enthalpy

For the equilibrium properties of the pure working fluid water the IAPWS-97 formulation (Wagner et al. 2000) is used in an implementation for Excel (Holmgreen 2007).

Assuming water as ideal gas and neglecting temperature dependencies of the molar reaction enthalpy ΔH_R and entropy ΔS_R, the equilibrium properties of the hydration reaction Eq [1] can be calculated with the modified Van't Hoff equation

$$ln\left(\frac{p}{p^{\circ}}\right) = \frac{\Delta S_s^{\circ}}{R} - \frac{\Delta H_s^{\circ}}{RT}, \qquad [2]$$

where the index ° denotes the standard state (25 °C, 1 bar).

The hydration enthalpy ΔH_s° (same for ΔS_s°) is the reaction enthalpy per mole of water ($\Delta H_s = \Delta H_R/\Delta n$), i.e. the change in enthalpy of the system per amount of water bound from the gas phase.

The reaction enthalpy can easily be deduced from the reactants' standard enthalpies of formation ΔH_f°:

$$\Delta H_R^{\circ} = \Delta H_{f,M_aX_b\cdot mH_2O}^{\circ} - \left[\Delta H_{f,M_aX_b\cdot nH_2O}^{\circ} + \Delta n \Delta H_{f,H_2O(g)}^{\circ}\right]. \qquad [3]$$

The same applies for ΔS_R°, which may need to be computed from Gibbs free enthalpies ($\Delta S_f^{\circ} = T^{\circ}\Delta H_f^{\circ} - T^{\circ}\Delta G_f^{\circ}$). For many compounds values for ΔH_f° and ΔG_f° (or ΔS_f°) are available from the literature or from chemical databases. In this work the extensive database of almost 300 salt hydrate pairs published by Glasser (2014) (widely based on HSC HSC Chemistry 2009 and Lide 2006) is used for most reactions.

2.3 Assessment parameters

The assessment is based on the equilibrium properties given as characteristic temperature difference, the coefficient of performance on material level and the mass-related energy storage density.

2.3.1 Characteristic temperature difference

Temperatures and pressures at which the processes take place are coupled through the saturation pressure curves of the used hydration reaction and the pure working fluid (see Figure 1). As temperature boundary conditions arise from application, suitable hydration reactions have to be chosen. With the saturation temperature $T_{s,sat}(p)$ or pressure $p_{s,sat}(T)$ according to Eq [2] the characteristic temperature difference

$$\Delta T_{ch}(p) = T_{s,sat}(p) - T_{wf,sat}(p) \quad \text{or} \quad \Delta T_{ch}(T_s) = T_s - T_{wf}\left(p_{s,sat}(T_s)\right) \qquad [4]$$

may be used to characterize the hydration reactions suitability for a given application. For convenience ΔT_{ch} is given as a function of the salt hydrate temperature T_s. Its direct relation to the applications' boundary temperature conditions provides higher practicability than mere saturation pressure curves. Moreover, the characteristic temperature difference ΔT_{ch} is only little dependent on p (resp. T_s) for most reactions under practical conditions. Here ΔT_{ch} is calculated for T_s = 50 °C and 100 °C written as $\Delta T_{ch,50}$ and $\Delta T_{ch,100}$.

In addition to ΔT_{ch}, driving temperature differences and differences between in- and outlet temperature of the HX-fluid have to be taken into account for any real application. They are required to overcome heat and mass transfer resistances and to exchange heat at finite HX-fluid flow. The driving forces may be gradients in temperature, pressure, concentration and/or chemical potential. In terms of temperature levels the driving forces manifest as an increased temperature difference during dehydration (higher temperature for dehydration and lower temperature for condensation with respect to equilibrium temperature levels) and a decreased temperature difference during rehydration (lower temperature for rehydration and higher temperature for evaporation). The actual level of increase depends on design (heat exchanger (HX) geometry & material, material porosity, vapor channels, supporting structures, etc.) and operation (power density, flow rates and inlet-outlet temperature differences of the heat exchanger fluids, absolute temperature levels, cycle lengths, etc.). Under practical conditions total increases are in the range of 5 to 20 K.

Several consecutive hydration reactions may be combined to multi-step cycles. Then, the temperature differences of dehydration and rehydration are determined by the (greatest) ΔT_{ch} of the lowest hydration step and the (smallest) ΔT_{ch} of the highest hydration step.

2.3.2 Coefficient of performance

As upper boundary to any possible cycle efficiency the ideal coefficient of performance of the ideal heat pump cycle (see above) on material level is evaluated. This reference cycle is based on the following:

1. Yield of useful heat on one temperature level: $T_{cnd} = T_{reh} = 50$ °C,
2. Ideal heat and mass transfer: no additional temperature differences,
3. Enthalpies of hydration and evaporation as well as heat capacities are assumed constant and evaluated at $T°$: temperature dependency neglected,
4. Balance only on material level: neglected all materials other than the working pair (e.g. supporting structure, heat exchangers, tubing, housing, insulation).

With these assumption and the amounts of heat according to Figure 1, the coefficient of performance is

$$COP_h = \frac{Q_{cnd} + Q_{reh} + Q_{sens,s,dry}}{Q_{deh} + Q_{sens,s,wet}} \approx \frac{\Delta n\left(\Delta H_v^{\circ} + \Delta H_s^{\circ}\right) + c_{p,m,s,dry}^{\circ}\Delta T_{ch,deh}}{\Delta n \Delta H_s^{\circ} + c_{p,m,s,wet}^{\circ}\Delta T_{ch,deh}}, \qquad [5]$$

with $\Delta n_{wf} = \Delta n \cdot n_s$ and the definition of the characteristic temperature difference ΔT_{ch} Eq [4]. The dehydration temperature is: $T_{deh} = T_{reh} + \Delta T_{ch}(T_{deh})$. The molar heat capacities of the lower and the upper hydration level $c_{p,m,s,dry}^{\circ}$ and $c_{p,m,s,wet}^{\circ}$ are estimated using Kopp's rule (Liley et al. 1999). The inherent error of this method in the order of 10% is tolerated given the scarcity of experimental values for many salt hydrates, the little sensitivity of Eq [5] to $c_{p,m,s}^{\circ}$ and the unavoidable coarsness of this material screening.

2.3.3 Energy storage density

As indicator for the energy storage density the amount of heat released at rehydration is related to the mass of upper hydrate:

$$q_{reh} = \frac{Q_{reh}}{m_{s,wet}} \approx \frac{\Delta n \Delta H_s^{\circ}}{M_{s,wet}}. \qquad [6]$$

In any application the salt hydrate is only a part of the total mass of the storage apparatus, hence storage densities might be about 1/3 to 1/10 of q_{reh}. The volumetric storage density can be deduced from q_{reh} using the material density and porosity.

2.4 Included reactions

The assessment is based on the database of 294 salt hydrate reactions published by Glasser (2014) and extended by the 17 salt hydrates included in N'Tsoukpoe's (2014) second screening step. Compounds are excluded a priori that contain rare earth metals[1], radioactive elements (Ra, U or Pu) or precious metals (Ag or Au),

1. have obvious economic limitations (not available[2] at Sigma-Aldrich or only at > 500 €/kg$_{\mathrm{anh}}$[3]),
2. are known to not form any stable hydrate at all ($BaSO_4$, CaF_2, K_2SO_3, K_2SO_4, KBr, KCl) or where (de)hydration is known to be strongly irreversible (Al_2O_3),
3. where the salt itself is unstable at 50 °C or below (e.g. forming gases or exploding) (Al_4C_3, $Ba(N_3)_2$, $MgCO_3$, $MgCO_3$, $NaHCO_3$), or
4. are mutagenic (GHS H34x), carcinogenic (H35x), very toxic (GHS H300, H301, H310, H311, H330, H331), very corrosive (H314), very environmentally harmful (H400, H410) or oxidizing (H271, H272)[4].

Moreover, reactions were excluded if the higher hydration level is known to be melting below 50 °C, because of the associated practical limitation for storage and transport[5]. Reactions including metastable hydration levels[6], where intermediate hydration levels are unclear/not taken into account[7] or that have values for ΔH_f° or ΔS_f° missing or suspicious[8] could not be included but might be of later interest. In total the assessment parameters are evaluated for 34 remaining hydration reactions.

3 RESULTS AND DISCUSSION

The results of the assessment of 25 reactions are summarized in Table 1. All (n = 9) reactions with $\Delta T_{ch,50} < 20$ K were disregarded[9] as they would hardly provide any useful effect considering temperature differences for heat and mass transfer (cf. 2.3.1).

For some compounds only information on the stability at certain temperatures could be found, indicating that the melting point of the higher hydrate T_{mlt} must be greater or equal (consequently for $T_{cnd,max}$).

For some reactions the condensation temperature of the reference cycle ($T_{cnd} =$ 50 °C) is higher than T_{mlt}, i.e. the reference cycle would fail by melting the salt hydrate. In these cases values for COP$_h$ and q_{reh} are theoretical extrapolations. However, they remain useful because the effect of the absolute temperature level of the cycles is usually small as the comparison of $\Delta T_{ch,50}$ and $\Delta T_{ch,100}$ shows. It should be noted that the assumption of temperature invariance for calculating the equilibria (Eq [2]) becomes weak for high values of ΔT_{ch} and results should be regarded as indicative only.

COP$_h$ is mainly depending on ΔT_{ch} (cf. Eq [5]) with outliers in the $CaCl_2$ hydrates. For these Glasser (2014) gives vapor pressures above pure water which is implausible and inconsistent with the experimental work cited by N'Tsoukpoe et al. (2015). Therefore, values derived from the latter were used. However, they should be treated cautiously given the high COP$_h$-values and the striking variation in ΔT_{ch}.

Even though restricted to less than 500 €/kg, prices vary by one order of magnitude and remain a relevant selection criterion depending on the economics of the application. However, the prices mentioned are only of comparative value and may not be used to judge economic viability of applications.

Interesting candidates for e.g. gas fired heat pumps for space heating with external temperature levels of -10 °C, 50 °C and 140 °C for ambient source, heating system and heat source respectively may be

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[1] Sc, Y, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu

[2] $BaAl_2O_4$, $CaSeO_4$, $CaSiF_6$, $CaSO_3$, $CaTeO_3$, $CsAl(SO_4)_2$, $Cu(IO_3)_2$, $Cu_3(PO_4)_2$, $CuHPO_4$, K_2CuCl_4, K_2OTiO_2, $LiNO_2$, $MgSeO_3$, $MgSeO_4$, $MgSO_3$, $MgTeO_3$, $MnSeO_4$, Na0.96Al0.96Si2.04O6, $Ni(IO_3)_2$, $Sr(BrO_3)_2$, $Sr(IO_3)_2$, $SrTeO_3$, $Th(NO_3)_4$, $TiOSO_4$

[3] $Ba(IO_3)_2$, $BaBr_2$, BaI_2, $CoBr_2$, $Cr_2(SO_4)_3$, $CrCl_2$, Cs_2CO_3, CsCl, $CuSeO_3$, $LiBO_2$, LiI, $LuCl_3$, $MnBr_2$, MnF_2, MnI_2, $PrCl_3$, $PtCl_4$, Rb_2CO_3, $RbAl(SO_4)_2$, RbF, RbOH, $SrBr_2$, Tc_2O_7, ThF_4, $VOSO_4$, ZnF_2

[4] Na_2S (H301, H311, H314, H400) is included due to its application in the EU FP7 project *MERITS*

[5] $CaBr_2\cdot(2\text{-}6)H_2O$, $CaCl_2\cdot(4\text{-}6)H_2O$, $CaCl_2\cdot(2\text{-}4)H_2O$, $LiBr\cdot(2\text{-}3)H_2O$, $CaHPO_4\cdot(0\text{-}2)H_2O$, $LiCl\cdot(1\text{-}2)H_2O$, $LiBr\cdot(1\text{-}2)H_2O$, $MgSO_4\cdot(6\text{-}7)H_2O$, $MnSO_4\cdot(5\text{-}7)H_2O$, $Na_2CO_3\cdot(1\text{-}7)H_2O$, $Na_2CO_3\cdot(7\text{-}10)H_2O$, $Na_2HPO_4\cdot(2\text{-}7)H_2O$, $Na_2HPO_4\cdot(7\text{-}12)H_2O$, $Na_2S_2O_3\cdot(0\text{-}5)H_2O$, $Na_2SO_3\cdot(0\text{-}7)H_2O$, $Na_2SO_4\cdot(0\text{-}10)H_2O$, $Na_2SO_4\cdot(7\text{-}10)H_2O$, $Na_2S\cdot(5\text{-}9)H_2O$

[6] $MnSO_4\cdot(1\text{-}4)H_2O$, $Na_2SO_4\cdot(0\text{-}7)H_2O$, $Na_2SO_4\cdot(7\text{-}10)H_2O$

[7] $Al_2(SO_4)_3\cdot xH_2O$, $AlF_3\cdot(0.5\text{-}3)H_2O$, $Ca(CH_3COO)_2\cdot xH_2O$, $CaSO_4\cdot(0.5\text{-}2)H_2O$, $FeCl_3\cdot(0\text{-}6)H_2O$, $K_3PO_4\cdot(0\text{-}7)H_2O$, $K_4P_2O_7\cdot(0\text{-}3)H_2O$, $Mg_3(PO_4)_2\cdot xH_2O$, $MgSO_4\cdot(1\text{-}4)H_2O$, $Na_2B_4O_7\cdot(0\text{-}10)H_2O$, $Na_2S_2O_3\cdot(0\text{-}5)H_2O$

[8] $FePO_4\cdot(0\text{-}2)H_2O$, $SrCl_2\cdot(0\text{-}1)H_2O$, $SrCl_2\cdot(1\text{-}2)H_2O$

[9] $FeSO_4\cdot(1\text{-}4)H_2O$, $NaBr\cdot(0\text{-}2)H_2O$, $FeSO_4\cdot(4\text{-}7)H_2O$, $Na_4P_2O_7\cdot(0\text{-}10)H_2O$, $MgSO_4\cdot(4\text{-}6)H_2O$, $Na_2HPO_4\cdot(0\text{-}2)H_2O$, $SrCl_2\cdot(2\text{-}6)H_2O$, $Na_2WO_4\cdot(0\text{-}2)H_2O$, $FeCl_2\cdot(2\text{-}4)H_2O$

Table 1: Results of assessed hydration reactions sorted by their characteristic temperature difference, red entries: not possible as dehydration T_s = 100 °C ($\Delta T_{ch,100}$) or with T_{cnd} = 50 °C (q_{reh}, COP$_h$) would melt the material (sources of equilibria and T_{mlt} by letters[10] or (Glasser 2014))

Hydration reaction	T_{mlt} °C	$T_{cnd,max}$ °C	$\Delta T_{ch,50}$ K	$\Delta T_{ch,100}$ K	q_{reh} kJ/kg$_{wet}$	COP$_h$ -	Price €/kg$_{anh}$
$KAl(SO_4)_2\cdot(3\text{-}12)H_2O$	93[d]	80.2	20	10	1062	1.76	218
$Na_2CO_3\cdot(0\text{-}1)H_2O$	109-149[e]	≥102	23	11	479	1.70	29
$NaHSO_4\cdot(0\text{-}1)H_2O$	59[e]	36	23	20	379	1.78	26
$AlNH_4(SO_4)_2\cdot(0\text{-}12)H_2O$[a]	94[f]	76	25	16	1518	1.74	125
$Li_2SO_4\cdot(0\text{-}1)H_2O$	234[e]	220	43	42	447	1.67	191
$FeCl_2\cdot(0\text{-}2)H_2O$	118[e]	89	44	35	808	1.62	175
$KAl(SO_4)_2\cdot(0\text{-}3)H_2O$	≥113[g]	≥75	45	41	594	1.65	218
$CaCl_2\cdot(1\text{-}2)H_2O$[b]	176[b]	*100*	*48*	*59*	*323*	*1.82*	110
$K_2CO_3\cdot(0.5\text{-}1.5)H_2O$	130-136[e]	≥91	49	45	385	1.60	49
$MgCl_2\cdot(4\text{-}6)H_2O$	116[h]	65	50	51	573	1.65	46
$K_4Fe(CN)_6\cdot(0\text{-}3)H_2O$	87[e]	28	51	62	357	1.70	71
$Ca(H_2PO_4)2\cdot(0\text{-}1)H_2O$	≥100[d]	≥36	55	64	211	1.59	70
$Na_2S\cdot(2\text{-}5)H_2O$[c]	83[c]	27	55	56	1124	1.62	204
$LiCl\cdot(0\text{-}1)H_2O$	96[i]	32	60	64	1041	1.61	148
$Na_2S\cdot(0\text{-}2)H_2O$[c]	83[c]	21	63	59	1297	1.54	204
$CaCl_2\cdot(0\text{-}1)H_2O$[b]	187[b]	*62*	*64*	*86*	*334*	*1.76*	110
$K_2CO_3\cdot(0\text{-}0.5)H_2O$	≥130[e]	≥51	74	80	238	1.45	49
$LiBr\cdot(0\text{-}1)H_2O$	156[i]	72	76	84	663	1.54	139
$MgCl_2\cdot(2\text{-}4)H_2O$	180[e]	91	77	87	811	1.53	46
$FeSO_4\cdot(0\text{-}1)H_2O$	≥300[j]	≥232	83	93	418	1.48	22
$MnSO_4\cdot(0\text{-}1)H_2O$	≥200[e]	≥97	84	96	411	1.49	24
$MgCl_2\cdot(1\text{-}2)H_2O$	235[e]	120	90	104	543	1.46	46
$MgBr_2\cdot(0\text{-}6)H_2O$	172[h]	42	98	114	1489	1.51	229
$MgCl_2\cdot(0\text{-}1)H_2O$	≤240[*,k]	≤40	128	148	737	1.34	46
$MgSO_4\cdot(0\text{-}1)H_2O$	≥400[k]	≥80	166	190	780	1.22	87

* decomposes at this temperature (might start earlier)

$LiBr\cdot(0\text{-}1)H_2O$ or $MgCl_2\cdot(2\text{-}4)H_2O$. They have a sufficiently high melting point to allow high condensation temperatures and reasonable energy densities and COPs. With a $T_{ch,50}$ of 76 K and 77 K they would allow total driving temperature differences of roughly 15 K during dehydration and rehydration as a good basis for reasonable power density. Though, $MgCl_2$ would be the more cost effective choice.

For thermal energy storage applications the two step cycle $Na_2S\cdot(0\text{-}2)H_2O$+$Na_2S\cdot(2\text{-}5)H_2O$ provides the attractive storage density of 2004 $\mathrm{kJ/kg_{Na_2S\cdot 5H_2O}}$. The highest safe fluid inlet temperature for dehydration is 83 °C. With an assumed total driving temperature difference of 10 K this results in a condenser inlet temperature of not more than 21 °C – 10 K = 11 °C for the second step ($Na_2S\cdot(0\text{-}2)H_2O$). This temperature level would need to be provided by an ambient heat sink when charging the storage. When discharging the storage with an assumed ambient heat source providing 5 °C at evaporator inlet, the heat would be released to the heating system at a temperature level of about 5 °C + 55 K – 10K = 50 °C at the second step ($Na_2S\cdot(2\text{-}5)H_2O$). The "temperature loss" during storage would be 33 K.

4 CONCLUSION

Based on the results of this assessment most suitable candidates may be identified by temperature requirements of the targeted application, economic considerations etc. These should undergo further in depth analysis to verify the data mentioned here (including a more thorough description of saturation properties) and extend it in terms of stability or reaction kinetics.

For some reactions a low max. condensation temperature $T_{cnd,max}$ showed to restrict their applicability considerably. In thermal storage applications $T_{cnd,max}$ restricts the temperature of the ambient heat sink

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[10] a: Wagman et al. 1982; b: N'Tsoukpoe et al. 2015; c: Boer et al. 2003; d: IFA 2016; e: Gmelin-Institut 1922ff; f: Helmboldt et al. 2007; g: Grønvold, Meisingset 1982; h: Patnaik 2003; i: Pátek, Klomfar 2006; j: Wildermuth et al. 2000; k: Seeger et al. 2011

(or source) when charging (or discharging) the storage. It will have to be 5-20 K below $T_{cnd,max}$ as additional driving temperature differences are required to allow for an acceptable (dis)charging power. As shown for the case of $Na_2S\cdot(0\text{-}2)H_2O$, this can be a major challenge for practical applications. Similarly, for heat pump or cooling cycles, $T_{cnd,max}$ restricts the temperature levels of the heating system or the heat rejection, respectively. It becomes obvious that storage density alone is not a sufficient indicator for a suitable material for thermochemical storage, nor is COP for heat pumping or cooling applications.

The approach may also be used to find suitable materials for further cycle options like cycles between different salt hydrates or multi-effect cycles. Also a direct comparison with cycles based on other working fluids like ammonia or alcohols is possible as the evaluation is independent of the pressure levels.

5 REFERENCES

Aristov, Y. I. (2013): Challenging offers of material science for adsorption heat transformation: A review. In *Applied Thermal Engineering* 50 (2), pp. 1610–1618. DOI: 10.1016/j.applthermaleng.2011.09.003.

Boer, R. de; Haije, W.G; Veldhuis, J.B.J (2003): Determination of structural, thermodynamic and phase properties in the Na2S–H2O system for application in a chemical heat pump. In *Thermochimica Acta* 395 (1–2), pp. 3–19. DOI: 10.1016/S0040-6031(02)00158-2.

Glasser, Leslie (2014): Thermodynamics of Inorganic Hydration and of Humidity Control, with an Extensive Database of Salt Hydrate Pairs. In *Journal of Chemical & Engineering Data* 59 (2), pp. 526–530. DOI: 10.1021/je401077x.

Gmelin-Institut für Anorganische Chemie und Grenzgebiete (Ed.) (1922ff): Gmelin-Handbuch der anorganischen Chemie. 8. Auflage.

Gordeeva, L. G.; Aristov, Yu I. (2012): Composites ‘salt inside porous matrix’ for adsorption heat transformation: a current state-of-the-art and new trends. In *International Journal of Low-Carbon Technologies* 7 (4), pp. 288–302. DOI: 10.1093/ijlct/cts050.

Grønvold, Fredrik; Meisingset, Knut K. (1982): Thermodynamic properties and phase transitions of salt hydrates between 270 and 400 K I. NH4Al(SO4)2 · 12H2O, KAl(SO4)2 · 12H2O, Al2(SO4)3 · 17H2O, ZnSO4 · 7H2O, Na2SO4 · 10H2O, and Na2S2O3 · 5H2O. In *The Journal of Chemical Thermodynamics* 14 (11), pp. 1083–1098. DOI: 10.1016/0021-9614(82)90152-5.

Hallström, Olof; Füldner, Gerrit; Spahn, Hans-Joseph; Schnabel, Lena; Salg, Frank (2014): Development of Collector Integrated Sorption Modules for Solar Heating and Cooling: Performance Simulation. In *Proceedings of the 2nd International Conference on Solar Heating and Cooling for Buildings and Industry (SHC 2013)* 48, pp. 67–76. DOI: 10.1016/j.egypro.2014.02.009.

Helmboldt, Otto; Keith Hudson, L.; Misra, Chanakya; Wefers, Karl; Heck, Wolfgang; Stark, Hans et al. (2007): Aluminum Compounds, Inorganic: Wiley-VCH (Ullmann's encyclopedia of industrial chemistry, 2). Available online at http://onlinelibrary.wiley.com/doi/10.1002/14356007.a01_527.pub2/full.

Holmgreen, Magnus (2007): X Steam. Version 2.5. Available online at http://xsteam.sourceforge.net/, checked on 2/6/2016.

HSC Chemistry. Version 7 (2009). Espoo (Finland): Outotec Research Oy.

Institute for Occupational Safety and Health (IFA) (2016): GESTIS Substance Database. Available online at http://gestis.itrust.de/, checked on 2/25/2016.

Lide, David R. (2006): CRC handbook of chemistry and physics. A ready-reference book of chemical and physical data. 87th ed. Boca Raton, Fla.: CRC Taylor & Francis.

Liley, Peter E.; Thomson, George H.; Friend, D. G.; Daubert, Thomas E.; Buck, Evan (1999): Section 2: Physical and Chemical Data. In : Perry’s chemical engineers’ handbook. 7th ed. New York, NY: McGraw-Hill.

N’Tsoukpoe, Kokouvi Edem; Rammelberg, Holger Urs; Lele, Armand Fopah; Korhammer, Kathrin; Watts, Beatriz Amanda; Schmidt, Thomas; Ruck, Wolfgang K. L. (2015): A review on the use of calcium chloride in applied thermal engineering. In *Applied Thermal Engineering* 75, pp. 513–531. DOI: 10.1016/j.applthermaleng.2014.09.047.

N'Tsoukpoe, Kokouvi Edem; Schmidt, Thomas; Rammelberg, Holger Urs; Watts, Beatriz Amanda; Ruck, Wolfgang K. L. (2014): A systematic multi-step screening of numerous salt hydrates for low temperature thermochemical energy storage. In *Applied Energy* 124, pp. 1–16. DOI: 10.1016/j.apenergy.2014.02.053.

Pátek, J.; Klomfar, J. (2006): Solid–liquid phase equilibrium in the systems of LiBr–H2O and LiCl–H2O. In *Fluid Phase Equilibria* 250 (1–2), pp. 138–149. DOI: 10.1016/j.fluid.2006.09.005.

Patnaik, Pradyot (2003): Handbook of inorganic chemicals. New York: McGraw-Hill (McGraw-Hill handbooks).

Seeger, Margarete; Otto, Walter; Flick, Wilhelm; Bickelhaupt, Friedrich; Akkerman, Otto S. (2011): Magnesium Compounds. Magnesium Compounds: Wiley-VCH (Ullmann's encyclopedia of industrial chemistry, 22). Available online at http://onlinelibrary.wiley.com/doi/10.1002/14356007.a15_595.pub2/full.

Solé, Aran; Martorell, Ingrid; Cabeza, Luisa F. (2015): State of the art on gas–solid thermochemical energy storage systems and reactors for building applications. In *Renewable and Sustainable Energy Reviews* 47, pp. 386–398. DOI: 10.1016/j.rser.2015.03.077.

Wagman, Donald D.; Evans, William H.; Parker, Vivian B.; Schumm, Richard H.; Halow, Iva; Bailey, Sylvia M. et al. (1982): The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C1 and C2 organic substances in SI units. Washington: ACS (Journal of physical and chemical reference data/Supplement, 11, 1982, 2). Available online at www.nist.gov/data/PDFfiles/jpcrdS2Vol11.pdf.

Wagner, W.; Cooper, J. R.; Dittmann, A.; Kijima, J.; Kretzschmar, H.-J.; Kruse, A. et al. (2000): The IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam. In *Journal of Engineering for Gas Turbines and Power* 122 (1), p. 150. DOI: 10.1115/1.483186.

Wildermuth, Egon; Stark, Hans; Friedrich, Gabriele; Ebenhöch, Franz Ludwig; Kühborth, Brigitte; Silver, Jack; Rituper, Rafael (2000): Iron Compounds: Wiley-VCH (Ullmann's encyclopedia of industrial chemistry, 20).

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