

Systematic search algorithm for potential thermochemical energy storage systems



Markus Deutsch^{a,*}, Danny Müller^b, Christian Aumeyr^b, Christian Jordan^a, Christian Gierl-Mayer^c, Peter Weinberger^b, Franz Winter^a, Andreas Werner^d

^a Institute of Chemical Engineering, Vienna University of Technology, 1060 Vienna, Austria

^b Institute of Applied Synthetic Chemistry, Vienna University of Technology, 1060 Vienna, Austria

^c Institute of Chemical Technologies and Analytics, Vienna University of Technology, 1060 Vienna, Austria

^d Institute for Energy Systems and Thermodynamics, Vienna University of Technology, 1060 Vienna, Austria

HIGHLIGHTS

- An automated search for reaction systems suitable for thermochemical energy storage was performed.
- Algorithm to build reaction systems for thermochemical energy storage is presented.
- Close to 1000 possible reaction systems for 5 different reactive gases were found.
- The VIENNA TCES-database for thermochemical energy storage materials is presented.

ARTICLE INFO

Article history:

Received 3 June 2016

Received in revised form 16 August 2016

Accepted 25 August 2016

Keywords:

Thermochemical energy storage

Database

Systematic search

Storage material

ABSTRACT

Thermochemical energy storage (TCES) is considered as an emerging green technology for increased energy utilization efficiency, thereby achieving a reduction of greenhouse gases. Various reaction systems based on different substance classes (e.g. hydrates, hydroxides, oxides) were suggested and investigated so far. Nevertheless, the number of known reactions which are suitable is still limited, as the main focus concentrates on the investigation of a handful known substances, their further improvement or applicability. To find novel promising candidates for thermochemical energy storage and also to allow for a broader view on the topic, this work presents a systematic search approach for thermochemical storage reactions based on chemical databases. A mathematical search algorithm identifies potential reactions categorized by the reactant necessary for the reaction cycle and ranked by storage density. These candidates are listed in the online available VIENNA TCES-database, combined with experimental results, assessing the suitability of these reactions regarding of e.g. decomposition/recombination temperature, reversibility, cycle stability, etc.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Research on the topic of thermochemical energy storage (TCES) has experienced an increased perception in the last few years. This is primarily driven by the possibility to reduce CO₂ emission by energy savings in buildings and industrial sectors and reducing waste thermal energy on a national and continental scale [1]. In this context TCES is of special interest due to its applicability in a wide temperature range and for a variety of applications.

The International Energy Agency (IEA) distinguishes three temperature levels for heat: low (<100 °C), medium (100–400 °C) and high (>400 °C) [2].

The low temperature level represents the typical household application. There, TCES can be used for heating and cooling, often in combination with solar energy [3].

The medium temperature level comprises mainly waste heat sources from industrial applications, which are a major cause of energy inefficiency [4]. Waste heat occurs when heat is used within production processes either in form of process steam or in fired furnaces [5]. In electricity production about 66% of the total primary energy input are lost during the conversion from heat to electricity [6]. A higher conversion rate to electricity is hampered by the comparably low efficiency of the available processes (e.g.

* Corresponding author.

E-mail address: markus.deutsch@tuwien.ac.at (M. Deutsch).

the energy efficiency of the organic rankine cycle (ORC) process at the cement plant in Lengfurt, Germany, is at only 12.8% [7]). The use of waste heat as heat itself is often not possible due to the fact that supply and demand cannot be matched temporally or the distances between producer and customer are too large [8]. TCES can be used to improve the energy efficiency of processes, by bridging the temporal and/or spacial gap between the producer of waste heat and potential consumer (e.g. from the heat production site to a local heating district or in a batch process, from the cool down of one cycle to the heat up of the next) [9].

In the high temperature level TCES can be used for specialized applications. In cars 60% of the fuel energy are lost as heat, mostly through the exhaust at a temperature up to 800 °C [10]. TCES can be used to recuperate parts of this energy and use it for minimizing the warm-up period of the exhaust track at the next cold start [11]. TCES can also be combined with concentrating solar plants to increase their production into times with low sunlight (e.g. when the sun is blocked by clouds or after sunset) [12,13]. For this application materials for temperatures of 800 °C or higher are needed.

TCES is based on a reversible chemical reaction (1). Heat is consumed, while decomposing material A into two products B and C, thus storing the reaction energy ΔH_R in the products. To discharge the system, both products B and C react under formation of A, now releasing the stored energy.



The direction of the reaction, which strongly depends on temperature, is given by the sign of the Gibbs energy ΔG_R :

$$\Delta G_R^T = \Delta H_R^T - T \Delta S_R^T \quad (2)$$

with $\Delta H_R^T = \sum_i v_i \Delta H_i^T$ and $\Delta S_R^T = \sum_i v_i \Delta S_i^T$, where ΔS_i^T being the reaction entropy (it can be assumed that $\Delta S_R > 0$ for the given notation of reaction (1)). If the reaction is in equilibrium then $T = T_{equ}$ and $\Delta G_R = 0$. For $T > T_{equ}$ follows that $\Delta G_R < 0$, which means the system reacts from left to right (decomposition), if $T < T_{equ}$ then $\Delta G_R > 0$ and the system reacts from right to left (recombination). The equilibrium temperature T_{equ} can be calculated iteratively from (2) by

$$T_{equ} = \frac{\Delta H_R^{T_{equ}}}{\Delta S_R^{T_{equ}}} = \frac{\sum_i v_i \Delta H_i^{T_{equ}}}{\sum_i v_i \Delta S_i^{T_{equ}}} \quad (3)$$

Since ΔH_i^T and ΔS_i^T differ for each substance, each reaction system has a specific T_{equ} . For an efficient use of TCES it is crucial that the equilibrium temperature of the applied reaction system fits to the temperature level of the heat source.

The fundamental process for TCES is depicted in Fig. 1. The charging reaction occurs in reactor 1, thereby decomposing the storage material A to B following reaction (1). Depending on the reaction system it may be necessary to store the produced gas C. The heat input is generally realized using a carrier gas. It is obligatory that the carrier gas is inert in terms of the reaction system, so no side reactions occur. The charged material B reacts with C back to A in reactor 2, releasing the previously stored energy. Again, in most processes a heat carrier gas will be used to transport the heat out of the reactor 2, which can be the reactive gas itself or an inert gas. It has to be noted that the temperature in reactor 1 T_1 has to be above T_{equ} of the reaction kinetic of the reaction system, while in reactor 2 it has to be vice versa ($T_2 < T_{equ}$) at the given process conditions. The required temperature spread $T_2 - T_1$ strongly depends on the reaction system and the process conditions. Reactors 1 and 2 can be located at different sites with a material transport system between them, e.g. trucks transporting the material. Another possibility would be to use only one reactor for both charging and discharging at different times in a batch process. Thus, on-site material storage would be needed for this case.

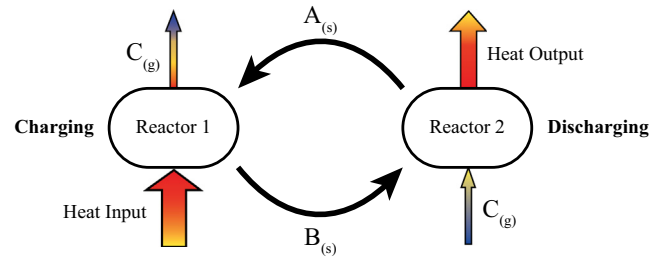


Fig. 1. Schematic principle of TCES.

There are various reaction systems in development at the moment. For the low and middle temperature level mainly salt hydrates [14], like $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}/\text{CaCl}_2$ [15,16] and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}/\text{MgSO}_4$ [17,18] are currently investigated. Pardo et al. [19] concluded that the most promising reaction systems for the high temperature level are $\text{Ca}(\text{OH})_2/\text{CaO}$ [20] and PbCO_3/PbO [21]. For solar applications, also reactions of metal oxides are shifting in the focus of the research [22,23].

The wide temperature range in which TCES can be utilized and the diversity of the reactions applicable for TCES create the necessity of a comprehensive database with different TCES reaction systems. This database helps the consumer to select an appropriate TCES reaction system for a given application purpose. The basis for such a database is a systematic screening to find reaction systems for a wide temperature range. So far, only one systematic approach to screen for TCES materials is known to the authors. N'Tsoukpoe et al. performed a systematic evaluation of 125 salt hydrates for TCES at low temperature levels with the main focus on a household application. They first discriminated based on material safety and past experiences, then focused on thermal analysis to find suitable candidates for TCES. The 125 salt hydrates were identified using a thermochemical database, but no detailed information on how they were identified was given [24]. In this work, reaction systems were identified for a broad temperature range (25–1000 °C). The use of an algorithm to find reaction systems results in an objective, comprehensive list, which is not based on prior knowledge of the researcher.

2. Search for potential storage systems

2.1. Goal of the search

With this systematic search approach for potential TCES systems the goal of the authors is the provision of an TCES database, where different kinds of principally suitable TCES reactions, sorted by temperature regime regarding their potential applicability, are listed. The entries in the database include products and educts of the reaction, equilibrium temperatures and, for selected promising candidates, also experimental data regarding material properties, reversibility of the TCES reaction, cycle stability and storage density. In a second step thermodynamic data and kinetic information will be supplemented. Below, the database search algorithm yielding potential TCES systems is described, for further details on the database see Section 3.

2.2. Basis of the search

The focus of this work lies on the search for potential TCES systems. In this first approach the search was narrowed to reactions of solid inorganic substances with a reactive gas, following general reaction



The focus on solid/gas reaction was done due to the fact that it is easy to separate the gaseous component from the solid one, ensuring energy storage over a long period by preventing reverse reaction. In contrast, for solid/liquid systems the separation is more energy consuming, resulting in a reduced storage capacity. Additionally, solid/liquid systems are contend with solubility of the solid reactants [25]. Furthermore only one gaseous component is allowed avoiding the need of a gas separation. The focus on inorganic substances was necessary due to the limitations of the search algorithm. While inorganic reactions can be identified by comparison of molecular formulas, for most organic reactions the structural formula of each reactant has to be considered. This would result in a steep increase in the complexity of the search algorithm and was therefore neglected in this approach.

2.2.1. Materials

In this first approach, building the basis of our database, a sum of 4528 different materials was taken into account as possible thermochemical energy storage materials. The thermodynamic data was gathered from HSC Chemistry data base [26].

2.2.2. Reactive gases

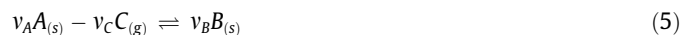
As outlined before our selection was limited to gas-solid reactions. The reactive gases in this work were limited to H₂O, CO₂, O₂, NH₃ and SO₂, as those are all commercially used reactive gases used on industrial scales. Additionally, risks and safety issues regarding handling and storage are known. Due to intrinsic problems on storage and handling H₂ was excluded as a reactive gas.

2.3. Search algorithm

To find reaction systems suitable for TCES, an algorithm was designed to find all possible reactions for a given set of materials. The algorithm identifies all possible decomposition reactions within the selected boundary conditions (maximal allowed stoichiometric coefficient) represented by reaction (4).

Fig. 2 shows a graphical visualization of the algorithm. It consists of 3 loops to determine the stoichiometric indices v_A (loop I), v_B (loop III) and v_C (loop II). In the following, the methodology is discussed and the determination of v_A , v_B and v_C is explained based on examples.

The concept behind the search algorithm is the rearrangement of a stoichiometric equation. From a mathematical point of view reaction (4) is identical to reaction (5).

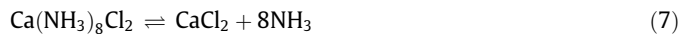


Hence, a stoichiometric correct reaction is obtained, if the subtraction of reactive gas C from substance A results in an elemental composition EC, for which a substance B can be found in the database.

In case of reaction (6), the subtraction of the elemental composition of H₂O (2H, 1O with 1 and 2 being the elemental indices) from the elemental composition of Mg(OH)₂ (1Mg, 2O, 2H) results in a composition (1Mg, 1O) which correlates to the database entry of magnesia oxide MgO.



To identify reactions which require multiple subtractions of C, (see reaction (7)) the stoichiometric coefficient v_C is increased incrementally until the subtraction is no longer possible (loop II). During each iteration, the resulting EC is checked against the database. A positive hit in the database is followed by the output of the corresponding substances as suitable TCES reaction. Subsequently or on a negative database request, the loop is repeated until the calculation of EC is no longer possible.



If a subtraction of v_C -times of C is not possible for the current v_C , the algorithm increases the stoichiometric coefficient v_A incrementally and starts again to subtract one C (loop I). This is necessary to find reactions like reaction (8), where more than 1 molecule of A is needed to obtain a balanced reaction equation with integers. Loop I is repeated until $v_A > v_{A,max}$ ($v_{A,max}$ is given by the user).



To identify reactions with $v_B \neq 1$, like reaction (9), the calculated EC of each subtraction is further analyzed in loop III (Fig. 3).



Therefore, the highest possible value for v_B , $v_{B,max}$, is determined based on the calculated elemental composition EC. In case of reaction (9) EC is 12Mn and 16O based on (5) with $v_A = 6$ and $v_C = 1$. $v_{B,max}$ is calculated as the lowest elemental index of EC, since it is the highest integer still able to divide EC without remainder. In this case $v_{B,max} = 12$ due to Mn.

To find all possible combinations, at first, a reaction with $v_B = 1$ is assumed. An intermediary elemental composition is calculated as $EC^* = EC/v_B$. EC^* is checked against the database to find a substance with a matching elemental composition. Then v_B is increased by one. If the division of all elemental indices of EC with the new v_B is possible without a remainder ($EC \bmod v_B = 0$), another possible elemental composition $EC^* = EC/v_B$ is found and subsequently checked against the database. This is repeated until $v_B > v_{B,max}$. For reaction (9) all possible v_B and the corresponding elemental compositions EC^* are given in Table 1. Only for $v_B = 4$ can a substance with a matching elemental composition (Mn₃O₄) be found in the database.

It should be noted, that this approach identifies all numerically possible reactions. The further discrimination of these hits regarding their chemical significance is given in Section 3.5.

3. Results

The search for each reactive gas was performed with $v_{A,max} = 6$ to cover reactions like reaction (9). For the five reactive gases (H₂O, CO₂, NH₃, SO₂, O₂) more than 1700 unique reactions were found. A comprehensive list of all reactions can be found on the project homepage.¹ For each reaction the equilibrium temperature T_{equ} has been calculated following (3) based on the thermodynamic data from HSC database.

For a reaction principally suitable as TCES system two criteria have to be met:

$$\Delta G_R^{25^\circ\text{C}} > 0 \quad (10a)$$

$$\Delta H_R^{T_{equ}} > 0 \quad (10b)$$

Criterion 1 (10a) defines the decomposition reaction for 25 °C as disfavoured, thus non-spontaneous. Therefore, at room temperature no decomposition will occur, which is obligatory for storage without energy loss. Criterion 2 (10b) follows the requirement that the reaction is endothermic at T_{equ} and therefore capable of storing energy while it decomposes.

Additionally, at this point only reactions with T_{equ} within the range of 25–2000 °C are considered relevant.

Thereby, the number of potential TCES systems is reduced to 1185 reactions. Table 2 gives the number of identified reactions per temperature level for each reactive gas based on T_{equ} . In Fig. 4 the distribution of the identified reactions is shown. The energy content is calculated as ΔH_R at T_{equ} for one kilogram of sub-

¹ solidheat.project.tuwien.ac.at.

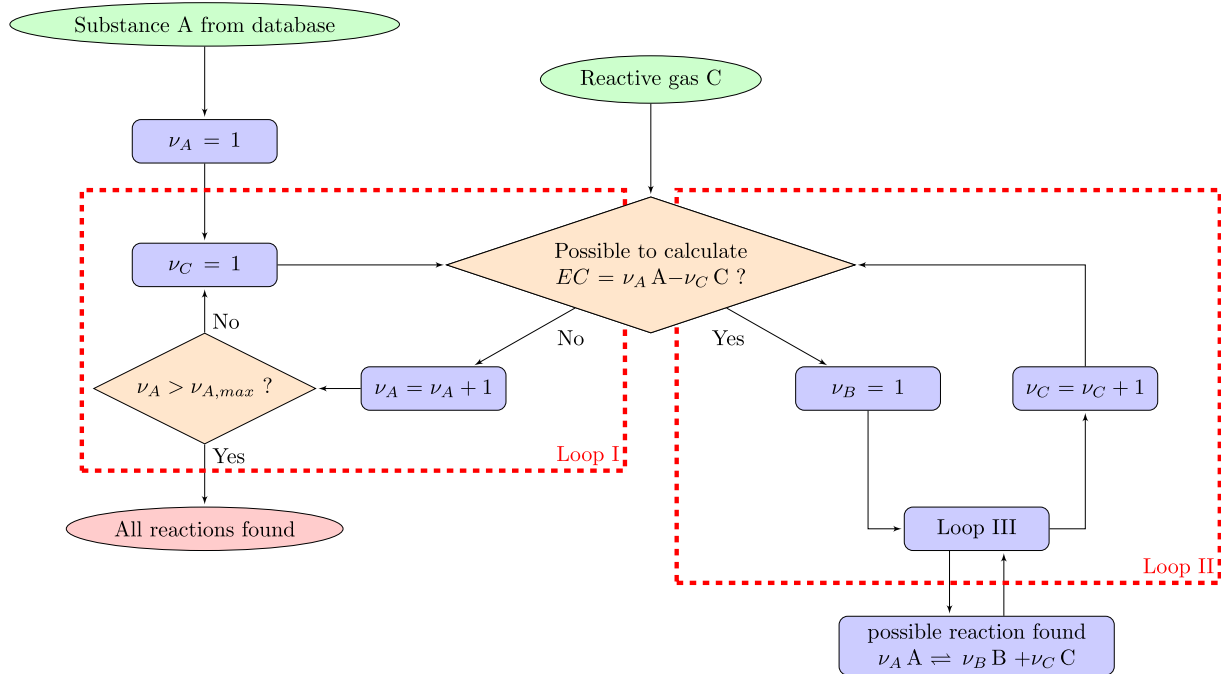


Fig. 2. Graphical representation of the search algorithm.

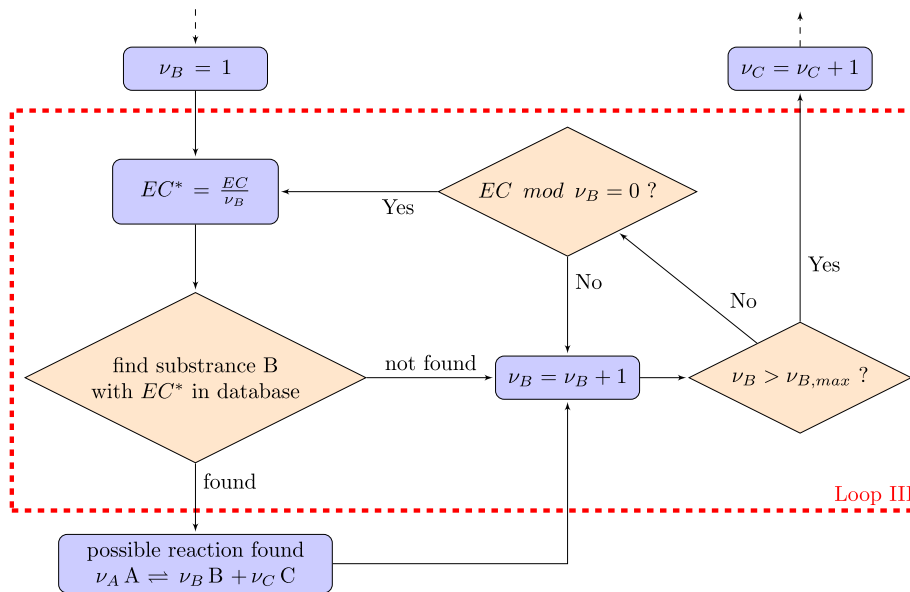


Fig. 3. Detailed graphical representation of loop III for the determination of ν_B .

Table 1
Possible elemental compositions EC^* for reaction (9) found in loop III.

ν_B	1	2	4
Mn	12	6	3
O	16	8	4

stance A of each reaction, therefore representing the theoretical energy amount stored in 1 kg material in its discharged state. Due to the high number of identified reactions with H_2O , those reactions are separated into reactions of hydroxides and metal hydrates.

A comparison of the different reactive gases is given in Fig. 5. The area for each gas marks the range where the majority of reactions are identified. To take into account that reactions with a higher T_{equ} are more sparse than with lower T_{equ} , as seen in Fig. 4, the reactions identified for each reactive gas were clustered. Fig. 6 shows the clustering exemplary for the reactions of hydroxides. First two clusters were calculated, utilizing *k-means* clustering based on the normed euclidean distances [27]. Then, from each cluster 80% of the reactions closest to the corresponding cluster centre are together surrounded by one convex hull. The line in Fig. 6 is equivalent to the line for H_2O -hydroxides in Fig. 5. In the following the identified reactions for different reactive gases are discussed further.

Table 2
Number of reactions identified with T_{equ} in the respective temperature level for each reactive gas.

	Temperature level of T_{equ}			Σ
	≤ 100 °C	100–400 °C	400 °C	
H ₂ O	203	321	29	553
CO ₂	1	22	17	40
NH ₃	15	20	4	39
SO ₂	0	2	26	28
O ₂	12	70	443	525
Σ	231	435	519	1185

3.1. Reactions with H₂O

The search with H₂O as reactive gas resulted in 553 identified reactions. They consist of reactions of metal hydroxides (47 reactions) and metal salt hydrates (506 reactions). The metal salt hydrates can be reduced to 206 decomposition reactions of different materials, excluding changes between different hydrate contents. As shown in Fig. 5, the reactions of metal salt hydrates mostly occur in a temperature range from room temperature to 500 °C, while the decomposition reactions of metal hydroxides can be found up to 1000 °C.

3.2. Reactions with CO₂

In total 40 reactions of CO₂ as reactive gas were identified. This class consists mainly of carbonates and a few oxalates, having equilibrium temperatures distributed over the whole temperature range.

3.3. Reactions with NH₃

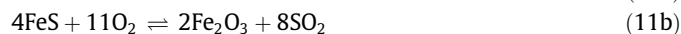
NH₃ as reactive gas yielded 39 decomposition reactions of 12 different metal salts, all of them having various coordination numbers of ammonia. The equilibrium temperatures are found between room temperature and 600 °C.

3.4. Reactions with SO₂

The search for reactions with SO₂ found 28 possible reactions, all reactions of metal oxides forming sulfates or sulfites. They are found in a temperature range between 400 and 1500 °C.

3.5. Reactions with O₂

Looking at reaction (11a) it is evident that due to the approach of the search algorithm reactions are identified which are stoichiometrically correct, but chemically they will not occur. For example, the oxidation of FeS with O₂ occurs according to reaction (11b), rather than (11a). But as reaction (11b) cannot be generalized via the approach of reaction (5), it is therefore not identified by the algorithm.



In order to reduce the number of reactions, which are stoichiometrically correct but chemically nonsense, they were separated into two classes. The first class included reactions where only O₂ and a metal are involved. This resulted in 248 reactions, which can be further divided into reactions involving an elemental metal (65 reactions) and reactions, where the solid components are both metal oxides, undergoing a change in the oxidation stage of metal (oxides) or the oxygen (peroxides) (overall 183 reactions). All these reactions are assumed to be chemically meaningful.

The second class includes reactions where oxygen, a metal and a non-metal element are involved (like (12)). It can be assumed that reactions where the oxidation number of the non-metal element changes from positive to negative can be eliminated for a first approach as they are more unlikely to occur. Reactions (12) illustrate this, as reaction (12b) is eliminated while reaction (12a) is kept. This leads to additional 104 reactions with O₂ for further investigation (173 reactions where removed).



4. Discussion

Using the HSC database as source for the systematic search algorithm, a notable list of reactions principally suitable as TCES materials was identified (see Section 3). This list is by no means complete, but reflects the general behaviour of the reactions with the different reactive gas. From Fig. 5 one can see that reactions systems of both H₂O-hydrates and NH₃ are limited to lower temperature levels. This results from the coordinative bond of H₂O and NH₃, respectively, which has a generally lower binding energy compared to covalent bonds of the reaction gases in other reaction systems. The lower binding energy induces a lower thermal stability, causing materials with coordinative bound H₂O or NH₃ to decompose earlier. On the other hand, materials that form covalent bonds are capable of forming multiple bonds per unit cell, e.g. MgSO₄·7H₂O can form 7 bonds per unit cell, thus storing the binding energy of a coordinative bond multiple times. The combination of both properties leads to high energy contents with low equilibrium temperatures, making both groups of reactions ideal for low temperature applications. Reactions of metal hydroxides seem to be disadvantageous compared to hydrate or amine reactions, due to their lower energy content, but since often not all coordinative bonds of hydrate or amines can be utilized for energy storage, metal hydroxides also pose possible options for TCES systems. For high temperature application, reactions with O₂, CO₂ and SO₂ are generally applicable, with the reactions with O₂ having an advantage in the realization as a result of the availability of O₂. To further discriminate the reactions for their suitability as a TCES system experimental investigation are necessary.

For selecting materials which would be suitable for a first experimental investigation the identified reactions were filtered according to following criteria:

1. reactions with a theoretical $T_{equ} < 1000$ °C
2. reactions with an energy density higher than 2 GJ/m³
3. reactions allowing for proper handling (thus avoiding liquid or molten decomposition products, unstable or highly corrosive reactants/products)

The first criterion was applied, since it is unlikely that heat with a temperature level above 1000 °C is available for storage. The sec-

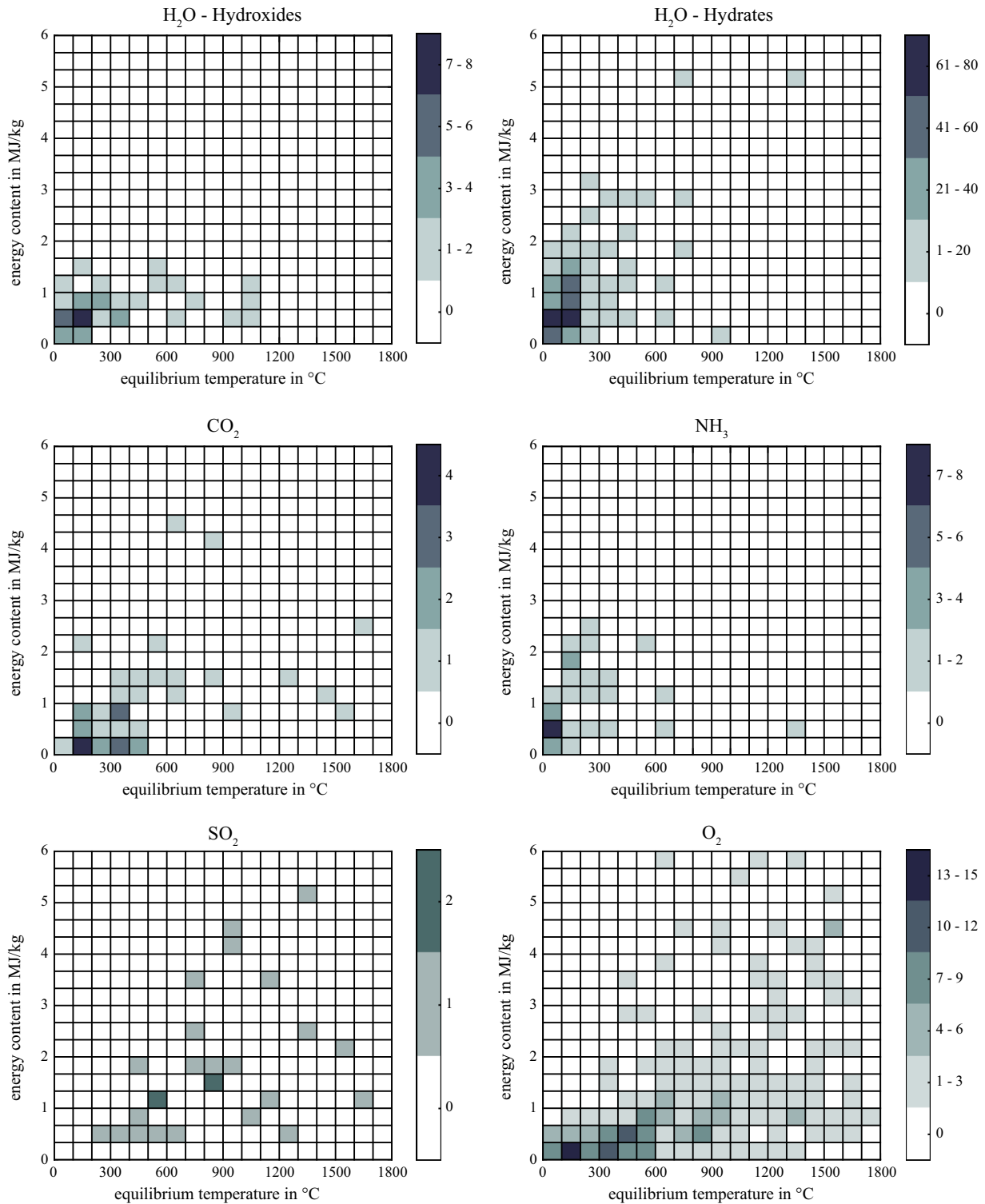


Fig. 4. Hit distribution maps for the different reactive gases. The colour corresponds to the number of reactions identified in the cell. Each cell has a width of 100 °C and a height of 0.33 MJ/kg. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ond criterion removes all systems with a low heat storage capacity since the heat storage capacity directly correlates with the economic feasibility of the system. Criterion 3 ensures that the found systems follow the general reaction (4). To a minor extent also availability, toxicity and finally the price were considered. Other properties like reversibility and cycle stability, which both are mandatory for a working TCES material, have to be checked indi-

vidually for each systems, since they cannot be calculated from thermodynamic data. Moreover, important characteristics of the system like the interaction with the containing material and sintering behaviour can only be assessed in context of a specific application. To further assess their real potential as TCES material, different analytical techniques were applied. Temperature dependent powder X-ray diffraction (P-XRD) under different (reactive

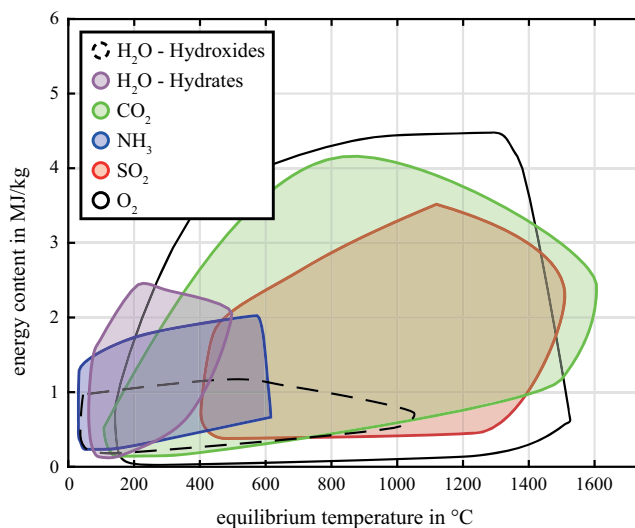


Fig. 5. Approximated areas within the majority of reactions have been found for each reactive gas.

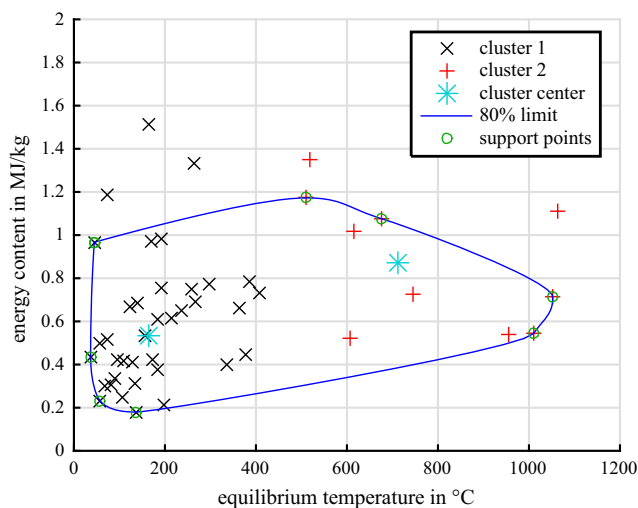


Fig. 6. Clustering of H₂O-hydroxide reactions into 2 clusters utilizing *k*-means clustering on normed euclidean distances. The blue line surrounds 80% of the reactions of each cluster and is calculated on the support points (○).

gas) atmospheres and simultaneous thermal analysis (STA) measurements, using comparable conditions, yielded information about decomposition and equilibrium temperatures, reversibility and nature of the intermediates and products. In case of reversibility, detailed measurements followed for better understanding of the undergoing processes, first kinetic information and also the determination of cycle stability. Finally, for the most promising candidates first runs in larger scales were performed. Reports on detailed investigations of the identified and investigated TCES materials will be published subsequently as full-papers.

5. Conclusion

The increased perception of TCES materials witnessed in the recent years stimulated the authors to look for a novel, systematic approach to this topic. Due to the so far limited number of investigated reactions the authors considered the provision of a database, allowing for a broader overview on principally suitable TCES reactions, as well as for a quick identification of the corresponding

parameters and experimental data. This could offer advantages for researchers and future industrial users as a variety of reactions, covering different temperature and reactive gas profiles are easily searchable.

The reactions entered in the VIENNA TCES-database are selected from chemistry databases; so far the HSC database was used as source. By the use of a systematic search algorithm potentially suitable candidates for TCES reactions were identified. The algorithm screens for reaction couples, where both educts and products have a database entry and can be matched via mathematical analysis of the corresponding elemental coefficients. Nevertheless, a control eliminating stoichiometric correct couples, where a reaction cannot occur, has to avoid chemically nonsense entries. According to this approach, and limited to gas-solid reactions, for a combination of five reactive gases led to 1012 principally suitable TCES materials (H₂O 553 hits, CO₂ 40 hits, NH₃ 39 hits, SO₂ 28 hits and O₂ 352 hits).

Those materials were filtered based on their equilibria temperature, energy density, reversibility and manageability. To further assess their potential as TCES material P-XRD and STA measurements were performed, which will be published subsequently as full papers.

Acknowledgements

The authors like to thank the Austrian Research Promotion Agency (FFG) for their financial support of the projects SolidHeat Basic (#841150), SolidHeat Kinetics (#848876) and GSG (#836636).

References

- [1] Arce P, Medrano M, Gil A, Oró E, Cabeza LF. Overview of thermal energy storage (TES) potential energy savings and climate change mitigation in Spain and Europe. *Appl Energy* 2011;88:2764–74.
- [2] IEA. Heating without global warming: market developments and policy considerations for renewable heat; 2014. <<http://www.iea.org>>.
- [3] Stitou D, Mazet N, Mauran S. Experimental investigation of a solid/gas thermochemical storage process for solar air-conditioning. In: 23rd International conference on efficiency, cost, optimization, simulation and environmental impact of energy systems. ECOS 2010, vol. 41. p. 261–70.
- [4] Chan CW, Ling-Chin J, Roskilly AP. A review of chemical heat pumps, thermodynamic cycles and thermal energy storage technologies for low grade heat utilisation. *Appl Therm Eng* 2013;50:1257–73.
- [5] Cot-Gores J, Castell A, Cabeza LF. Thermochemical energy storage and conversion: a-state-of-the-art review of the experimental research under practical conditions. *Renew Sustain Energy Rev* 2012;16:5207–24.
- [6] IEA. Co-generation and renewables: solutions for a low-carbon energy future; 2011. <<http://www.iea.org>>.
- [7] Brandstätter R. Industrielle abwärmenutzung, beispiel & technologien; 2008.
- [8] Ma Q, Luo L, Wang RZ, Sauer G. A review on transportation of heat energy over long distance: exploratory development. *Renew Sustain Energy Rev* 2009;13:1532–40.
- [9] Widhalm J, Fellner T, Deutsch M, Werner A, Winter F. Thermochemical energy storage as a way to increase the sustainability of energy generation. In: The international academic forum, editor. ACSEE2015 – official conference proceedings. p. 579–93.
- [10] Kata Y. Thermal energy storage in vehicles for fuel efficiency improvement. *Proc Effstock* 2009:14–7.
- [11] Chemical Heat Storage for Automotive Heating and Cooling Applications. In: 3rd IAV conference: thermoelectrics goes automotive, expert Verlag; 2012.
- [12] Romero M, Steinfeld A. Concentrating solar thermal power and thermochemical fuels. *Energy Environ Sci* 2012;5:9234–45.
- [13] Zaversky F, García-Barberena J, Sánchez M, Astrain D. Transient molten salt two-tank thermal storage modeling for CSP performance simulations. *Sol Energy* 2013;93:294–311.
- [14] Aydin D, Casey SP, Riffat S. The latest advancements on thermochemical heat storage systems. *Renew Sustain Energy Rev* 2015;41:356–67.
- [15] Korhammer K, Druske M-M, Fopah-Lele A, Rammelberg HU, Wegscheider N, Opel O, et al. Sorption and thermal characterization of composite materials based on chlorides for thermal energy storage. *Appl Energy* 2016;162:1462–72.
- [16] Fopah Lele A, Kuznik F, Rammelberg HU, Schmidt T, Ruck WKL. Thermal decomposition kinetic of salt hydrates for heat storage systems. *Appl Energy* 2015;154:447–58.

- [17] Hongois S, Kuznik F, Stevens P, Roux J-J. Development and characterisation of a new MgSO_4 -zeolite composite for long-term thermal energy storage. *Sol Energy Mater Sol Cells* 2011;95:1831–7.
- [18] Donkers PAJ, Beckert S, Pel L, Stallmach F, Steiger M, Adan OCG. Water transport in $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ during dehydration in view of thermal storage. *J Phys Chem C* 2015;119:28711–20.
- [19] Pardo P, Anxionnaz-Minvielle Z, Rougé S, Cognet P, Cabassud M. $\text{Ca}(\text{OH})_2/\text{CaO}$ reversible reaction in a fluidized bed reactor for thermochemical heat storage. *Sol Energy* 2014;107:605–16.
- [20] Nagel T, Shao H, Roßkopf C, Linder M, Wörner A, Kolditz O. The influence of gas–solid reaction kinetics in models of thermochemical heat storage under monotonic and cyclic loading. *Appl Energy* 2014;136:289–302.
- [21] Kato Y, Harada N, Yoshizawa Y. Kinetic feasibility of a chemical heat pump for heat utilization of high-temperature processes. *Appl Therm Eng* 1999;19:239–54.
- [22] Albrecht KJ, Jackson GS, Braun RJ. Thermodynamically consistent modeling of redox-stable perovskite oxides for thermochemical energy conversion and storage. *Appl Energy* 2016;165:285–96.
- [23] Carrillo AJ, Moya J, Bayón A, Jana P, La Peña O'Shea VA d, Romero M, et al. Thermochemical energy storage at high temperature via redox cycles of Mn and Co oxides: pure oxides versus mixed ones. *Sol Energy Mater Sol Cells* 2014;123:47–57.
- [24] N'Tsoukpoe KE, Schmidt T, Rammelberg HU, Watts BA, Ruck WKL. A systematic multi-step screening of numerous salt hydrates for low temperature thermochemical energy storage. *Appl Energy* 2014;124:1–16.
- [25] Solé A, Fontanet X, Barreneche C, Fernández AI, Martorell I, Cabeza LF. Requirements to consider when choosing a thermochemical material for solar energy storage. *Sol Energy* 2013;97:398–404.
- [26] Antti Roine. *Hsc chemistry*; 2007.
- [27] Hartigan JA, Wong MA. Algorithm as 136: a k-means clustering algorithm. *J R Stat Soc Ser C (Appl Stat)* 1979;28:100–8.