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Unified thermodynamic model to calculate COP of diverse sorption heat pump cycles: Adsorption, absorption, resorption, and multistep crystalline reactions[☆]

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ABSTRACT

A straightforward thermodynamic model is developed in this work to analyze the efficiency limit of diverse sorption systems. A method is presented to quantify the dead thermal mass of heat exchangers. Solid and liquid sorbents based on chemisorption or physical adsorption are accommodated. Four possible single-effect configurations are considered: basic absorption or adsorption (separate desorber, absorber, condenser, and evaporator); separate condenser/evaporator (two identical sorbent-containing reactors with a condenser and a separate direct expansion evaporator); combined condenser/evaporator (one salt-containing reactor with a combined condenser/evaporator module); and resorption (two sorbent-containing reactors, each with a different sorbent). The analytical model was verified against an empirical heat and mass transfer model derived from component experimental results. It was then used to evaluate and determine the optimal design for an ammoniate salt-based solid/gas sorption heat pump for a space heating application. The effects on system performance were evaluated with respect to different working pairs, dead thermal mass factors, and system operating temperatures. The effect of reactor dead mass as well as heat recovery on system performance was also studied for each configuration. Based on the analysis in this work, an ammonia resorption cycle using LiCl/NaBr as the working pair was found to be the most suitable single-effect cycle for space heating applications. The maximum cycle heating coefficient of performance for the design conditions was 1.50 with 50% heat recovery and 1.34 without heat recovery.

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1. Introduction

A natural gas-driven sorption heat pump for space heating applications was proposed and studied by Blackman et al. (2017) with the goal of reducing primary energy consumption and energy cost compared with conventional fuel-fired boilers and furnaces. The heat pump uses ammoniated salt or a salt pair to absorb ammonia refrigerant with three configuration options: the ammoniate adsorption cycle with separate condenser and evaporator (SCE), the ammoniate cycle with combined

Nomenclature

ADS	adsorption system
ABS	absorption system
COP	coefficient of performance
DTMR	dead thermal mass ratio, kJ kg^{-1}
L	latent heat, kJ kg^{-1}
Y	loading, kg^{-1}
Q	heat per unit of refrigerant, kJ kg^{-1}
T	temperature, $^{\circ}\text{C}$
m	mass, kg
ρ	density, kg m^{-3}
V	volume, m^3
ΔH	reaction heat, kJ kg^{-1}
ΔT	temperature difference, K
ΔY	differential loading, kg^{-1}
C_p	specific heat, $\text{kJ kg}^{-1} \text{K}^{-1}$
x	vapor quality
ε	heat exchange effectiveness
ψ	maximum cooling COP (ratio of latent heats defined in Table 1)
HTS	high temperature salt
LTS	low temperature salt
DTM	dead thermal mass, kJ K^{-1}
DTMR	dead thermal mass ratio
RES	resorption cycle
SCE	ammoniate adsorption cycle with separate condenser/evaporator
CCE	ammoniate adsorption cycle with combined condenser/evaporator
θ_1	Parameter associated with the dead thermal mass of the ΔT_L -coupled heat exchangers
θ_2	Parameter associated with the dead thermal mass of the ΔT_D -coupled heat exchangers
ε_1	sensible heat recovery fraction for ΔT_L -coupled heat exchangers
ε_2	sensible heat recovery fraction for ΔT_D -coupled heat exchangers
λ	COP approach factor
C/E	condenser/evaporator

Subscripts

0	low temperature heat source
1	medium temperature heat sink
2	high temperature heat source
D	desorber/difference
E	evaporator
L	lift
des	desorbing
$cond$	condensing
$comp$	ammonia complex
abs	absorbing
ads	adsorbing
$evap$	evaporating
ht	heating
cl	cooling
i	inlet
sol	solution
max	maximum
min	minimum
ref	refrigerant
ret	retained
liq	liquid
mat	material

HTF	heat transfer fluid
HTR	high temperature reactor
LTR	low temperature reactor
SHX	solution heat exchanger

condenser/evaporator (CCE), and the resorption cycle (RES). These configurations are the basic sorption cycle configurations in solid/gas chemisorption heat pump studies (Li et al., 2014; Wang et al., 2014; Wongsuwan et al., 2001). They are the foundation for various advanced cycles. Compared with the more advanced configurations of each type, they require the fewest components to develop a prototype machine (Blackman et al., 2017). To reveal the major characteristics of different cycle configurations, this study focused on these three basic configurations instead of other advanced ones.

The SCE cycle shown in Fig. 1a consists of two identical solid/gas reactors, a condenser, and an evaporator; the CCE cycle shown in Fig. 1b consists of a solid/gas reactor and a combined condenser/evaporator reactor; and the RES cycle shown in Fig. 1c consists of two solid/gas reactors. In the first half-cycle of operation, the heat pump is driven by natural gas where the heat evolving from a natural gas burner is used to desorb ammonia from the reactor to the condenser (SCE and CCE) or the reactor B (RES). The condensation (SCE and CCE) or reaction heat (RES) is used for space heating purposes. In the second half-cycle, the heat of adsorption from the reactor is used for heating purposes while an outdoor fan coil is thermally connected to the evaporator (SCE and CCE) or reactor B (RES) to absorb low-temperature thermal energy from outdoor air. It should be noted that the SCE studied in this work has two identical reactors running out of phase and simultaneously. One reactor is connected to the condenser, and the other is connected to the evaporator every half cycle. The condenser and evaporator run continuously.

Performance analysis and comparison of different configurations using various working pairs are necessary to determine the optimal design for prototype development. Moreover, the effect of dead thermal mass (or DTM, defined here as the sensible heat load $[\text{kJ K}^{-1}]$ due to the cyclic temperature swing of the sorbent, retained refrigerant, heat transfer fluid, and bed material) and different operating conditions should also be considered. In literature, the performance of various sorption cycles was analyzed by modeling and test approaches (Goetz et al., 1997; Zhu et al., 2016). Modeling is the faster and cheaper approach to evaluate a design. Three types of model are usually considered: thermodynamic model, lumped-parameter model, and distributed-parameter model (Pesaran et al., 2016). The thermodynamic model is the fastest and most straightforward model with acceptable error. It is always applied for fast preliminary analysis of sorption systems in many studies.

Thermodynamic studies of absorption cycle started from Carnot heat engine-heat pump model (Herold et al., 2016). Zebbar et al. (2012) applied exergy analysis to find irreversibility of a cycle. Optimizations were made based on that. Herold (1999) provided a zero-order model and compared calculated COP with real machine data. The model showed a more realistic result than reversible model. Xie and Jiang (2015) proposed a new absorption heat pump model based on ideal solution circulation. A temperature lift coefficient was connected to COP to illustrate basic performance of absorption heat pump.

Cacciola and Restuccia (1995) applied thermodynamic model based on first law analysis to calculate and compare the COP and cooling capacity of adsorption cycle with three different working pairs. Zeolite/water was concluded to be the most suitable

Fig. 1. Three possible sorption cycle configurations: (a) SCE, sorption with separate (dedicated) evaporator/condenser; (b) CCE, sorption with combined evaporator/condenser; and (c) RES, resorption.

pair for domestic applications in southern Europe. Meunier et al. (1998) defined entropic temperature and introduced equivalent Carnot cycle for thermodynamic modeling of sorption systems. Difference between liquid absorption and solid adsorption technologies was compared by internal entropy production calculation. Pons and Poyelle (1999) applied similar analysis to study two types of vapor recovery cycles. Dead thermal mass was not considered in the model. Douss and Meunier (1988) investigated the effect of operating temperatures on the COP of activated-carbon-methanol adsorption cooling systems with experimental test and a thermodynamic model. The model considered the extra sensible heat requirement of sorbent, refrigerant, and reactor metal under the desorption mode. Freni et al. (2015) developed a thermodynamic model to evaluate adsorption heat pump cycle with combined condenser-evaporator. Dead mass was considered in calculation of desorption and evaporation heat.

Li et al. (2014) provided a uniformed thermodynamic model to calculate performance of solid/gas sorption cycles. Sensible heat consumption was considered as a factor to improve cycle COP. However, the expression of sensible heat was too general that was unable to present key difference between cycles. Neveu and Castaing (1993) used thermodynamic model to compare performance of different solid/gas recovery cycles upgraded from SCE. Dead mass of material and heat transfer fluid were not considered. They also provided a three temperature model from first and second law of thermodynamics (Neveu, & Castaing, 1996). Sharma and Kumar (2017, 2018) applied thermodynamic model in metal hydride based sorption systems to choose suitable metal hydride pair. Material dead mass was considered. The author also considered mass transfer kinetics at different working pressures when selecting working pair candidates.

Present studies established a thermodynamic model for very specific cycles. It is hard to compare key difference between various cycles clearly. For simplification, some studies ignored dead thermal mass effect that would over evaluate the performance of system. Dead thermal mass is influenced by both design ability and inherent salt mass and should be discussed separately to better understand the improvement potential of the system. For fast preliminary analysis of sorption systems with many configuration and working pair options, and to facilitate qualitative comparison among such options, a thermodynamic model that is accurate, computationally efficient, and transparent in its technical meaning is needed.

In this work, a unified thermodynamic model for system COP of sorption cycles was developed to enable rapid performance comparison between, and analysis of, various cycle configurations and working pairs. A simple expression that accommodates ammoniate salt-based chemisorption and many other sorption cycle types was provided. A table was provided to clearly compare key differences

between systems: cycle configuration, working pair selection, and system design. Meanwhile, dead mass was considered in a new way that: (a) has separate terms for design-related and inherent mass, (b) is more relevant to cycle performance, and (c) is easier to compute.

2. Analytical model

An analytical model is developed in this section to evaluate the heating COP of various sorption cycle configurations. The following assumptions are made to simplify the model:

- Single effect cycles:** Only single effect cycles are considered, in order to reveal the major characteristics of different cycle configurations.
- Cyclic steady state:** The parameters (temperatures and refrigerant loading) at the end of a whole cycle are the same as those at the beginning of the cycle.
- Mass transfer temperature:** The desorption process happens only at T_{des} , the absorption/adsorption process happens only at T_{abs}/T_{ads} , and the evaporation process happens only at T_{evap} .
- Thermodynamic equilibrium:** Cycle time is not considered; it is assumed that processes reach equilibrium with no mass transfer limitations (solution leaves the desorber and absorber in equilibrium).
- No heat losses:** Losses through pipes and walls are neglected.
- Sorbent temperature:** References are made only to the sorbent bed temperatures (temperatures of external heat transfer fluids are not considered).
- Lumped capacitance:** The sorbent temperature is assumed to be spatially uniform.

2.1. COP expression for conventional absorption and adsorption cycles

In this work, the conventional absorption cycle is the basic single stage single effect absorption cycle that consists of a desorber, an absorber, a condenser, an evaporator, and optionally a solution heat exchanger (Herold et al., 2016). The conventional adsorption cycle refers to the basic adsorption cycle with a condenser, an evaporator, and one (or two) adsorption bed(s) as described by Wang et al. (2014). The conventional adsorption cycle is only differs from the SCE in Fig. 1 because the conventional adsorption cycle uses physical adsorption instead of chemisorption.

Analytical models for the cooling or heating COP of absorption and adsorption cycles have been proposed numerous times before; for example in Gluesenkamp (2012) and Freni et al. (2015). The heating COP of a sorption cycle is defined as the ratio between useful heat Q_1 and driving heat Q_2 , as shown in Eq. (1). It can also

be expressed in terms of low temperature source heat Q_0 and driving heat Q_2 .

$$COP_{ht} = \frac{Q_1}{Q_2} = 1 + \frac{Q_0}{Q_2} = 1 + COP_{cl} \quad (1)$$

For a sorption heat pump, the useful heat usually includes heat from both the absorber/adsorber and the condenser, and the driving heat is the heat into the desorber. Based on energy balance, the heating COP of a sorption heat pump can be expressed as one plus the ratio of evaporator heat to desorber heat—that is, one plus the cooling COP, had it been used as a chiller. Therefore, the following derivations will focus only on the evaporator heat and the desorber heat, which are defined as heat per unit mass flow of refrigerant.

For both absorption and adsorption cycles, the evaporator heat per unit mass flow of refrigerant can be expressed as Eq. (2). During cyclic steady state operation, only the latent heat of evaporation is considered. In the equation, $x_{evap,i}$ is the inlet vapor quality to evaporator, which depends on temperature lift $\Delta T_L = T_{cond} - T_{evap}$ and choice of refrigerant, as shown in Eq. (3).

$$Q_E = L_{evap}(1 - x_{evap,i}) \quad (2)$$

$$x_{evap,i} = \frac{C_{p,ref,liq} \Delta T_L}{L_{evap}} \quad (3)$$

The desorber heat is composed of the latent heat and the sensible heat. The latent heat is the main part of the heat requirement in desorber and is the same for absorption and adsorption cycles. The sensible heat is slightly different between absorption and adsorption cycles. For an absorption cycle, the sensible heating of the solution through the desorber is considered. The desorber heat is shown in Eq. (4). Note that Eq. (4) uses loading Y (i.e., the mass ratio of refrigerant to sorbent) instead of the convention more common for absorption systems (i.e., the mass fraction refrigerant for ammonia/water, or mass fraction sorbent for water/LiBr). The sensible heat depends on the inlet solution mass flow per unit mass flow of refrigerant, the driving temperature difference $\Delta T_D = T_{des} - T_{abs}$, the maximum loading in the desorber Y_{max} , the differential loading $\Delta Y = Y_{max} - Y_{min}$, and the effectiveness of the solution heat exchanger ε_{SHX} . The solution temperature difference can be calculated from $\Delta T_{sol} = (1 - \varepsilon_{SHX})\Delta T_D$, and the mass flow of solution per unit mass flow of refrigerant is $\frac{(1+Y_{max})}{\Delta Y}$. Then, by combining Eqs. (1)–(4), the heating COP for absorption cycle can be expressed as Eq. (5). Note that the use of Y_{max} is due to assumption c, which states that all desorption occurs at T_{des} . Thus all refrigerant in the sorbent at the end of sorption (associated with Y_{max}) must be sensibly heated in the transition from sorption to desorption.

$$Q_D = L_{des} + C_{p,sol}(1 - \varepsilon_{SHX})\Delta T_D \frac{(1 + Y_{max})}{\Delta Y} \quad (4)$$

$$COP_{ht} = 1 + \frac{L_{evap} - C_{p,ref,liq} \Delta T_L}{L_{des} + C_{p,sol}(1 - \varepsilon_{SHX})\Delta T_D \frac{(1 + Y_{max})}{\Delta Y}} \quad (5)$$

For an adsorption cycle, the desorption and adsorption processes occur separately in the same reactor. The sensible heat should include heating of the adsorbent, retained refrigerant, heat transfer fluid (HTF), bed material, and other possible “dead thermal masses” in the adsorber/desorber. Gluesenkamp (2012) defined a term dead thermal mass ratio (DTMR) to capture the relative size of these dead thermal masses. In this framework, the dead thermal mass (DTM), defined in Eq. (6a) is the aggregate of all thermal masses that must be heated and cooled each cycle. The DTMR is defined in Eq. (6b) as a dimensionless ratio of sensible heat to latent heat per cycle, including heat transfer fluid, heat exchanger materials, and the sensible heat of the sorbent and refrigerant. The

sensible heat per cycle is DTM [kJ K^{-1}] multiplied by ΔT_D [K], and the latent heat per cycle is the latent heat of desorption [kJ] per cycle. Note that the product of ΔY and m_{ads} give the mass of refrigerant transferred per half-cycle (also referred to as the active mass).

Using the DTMR, we can derive the heating COP for a typical adsorption cycle without heat recovery in Eq. (7). A more detailed expression that accounts for heat recovery is included in the work of Gluesenkamp (2012). Note that DTM is strictly a function of the geometry of the physical sorbent heat exchanger. As will be shown later, the impact of DTM on the cycle efficiency is mediated by DTMR, which also includes operating parameters (temperatures and working fluid properties).

$$DTM = \rho_{HTF} V_{HTF} C_{p,HTF} + \rho_{mat} V_{mat} C_{p,mat} + m_{ads}(C_{p,ads} + Y_{max} C_{p,ref,liq}) \quad (6a)$$

$$DTMR = \frac{\Delta T_D DTM}{\Delta Y m_{ads} L_{des}} \quad (6b)$$

$$COP_{ht} = 1 + \frac{L_{evap} - C_{p,ref,liq} \Delta T_L}{L_{des}(1 + DTMR)} \quad (7)$$

2.2. COP expression for ammoniate sorption with separate dedicated condenser and evaporator

In this section, the heating COP of an ammoniate sorption cycle with separate dedicated condenser and evaporator is derived. The expression for evaporator heat is the same compared with the conventional adsorption cycle. The desorber heat consists of both reaction heat and sensible heat. The reaction heat ΔH_{des} depends on the working pair and reaction process. The sensible heat is like that of the conventional adsorption cycle except that ammoniate composite instead of refrigerant is retained in the desorber. The DTMR and heating COP for ammoniate sorption cycle are shown in Eqs. (8) and (9).

$$DTMR = \frac{\Delta T_D}{\Delta Y m_{ads} \Delta H_{des}} (\rho_{HTF} V_{HTF} C_{p,HTF} + \rho_{mat} V_{mat} C_{p,mat} + (1 + Y_{max}) m_{ads} C_{p,comp}) \quad (8)$$

$$COP_{ht} = 1 + \frac{L_{evap} - C_{p,ref,liq} \Delta T_L}{\Delta H_{des}(1 + DTMR)} \quad (9)$$

2.3. COP expression for cycle with combined condenser/evaporator

The combined condenser/evaporator configuration can be used for both physical adsorption (such as water/silica gel) and chemical sorption (such as ammonia/ammoniated salts). The distinguishing characteristic of the CCE cycle is that a single chamber is used as the condenser in one half cycle and as the evaporator in the other half-cycle. This leads to two main differences compared with the conventional cycle. Firstly, the refrigerant will not go through an expansion process; therefore, the vapor fraction of the refrigerant at the beginning of evaporation is zero. Secondly, the dead thermal masses in the combined condenser/evaporator are cooled from T_{cond} to T_{evap} during the evaporation process, which reduces the evaporator heat and undermines the COP. The DTMR for evaporator and evaporator heat is shown in Eqs. (10) and (11). The $m_{ref,ret}$ is the retained mass of refrigerant at the end of the condensing process.

$$DTMR_E = \frac{\Delta T_L}{\Delta Y m_{ads} L_{evap}} (\rho_{HTF,E} V_{HTF,E} C_{p,HTF,E} + \rho_{mat,E} V_{mat,E} C_{p,mat,E} + m_{ref,ret} C_{p,ref,liq}) \quad (10)$$

Table 1
Expressions for characters in different systems.

System configuration	Abbr.	ψ	θ_1	θ_2
Absorption cycle	ABS	$\frac{L_{evap}}{L_{des}}$	$\frac{C_{p,ref,liq} \Delta T_L}{L_{evap}}$	$C_{p,sol} \Delta T_D \frac{(1 + Y_{min})}{\Delta Y_{L_{des}}}$
Adsorption cycle	ADS	$\frac{L_{evap}}{L_{des}}$	$\frac{C_{p,ref,liq} \Delta T_L}{L_{evap}}$	DTMR
Separate condenser/ evaporator cycle	SCE	$\frac{L_{evap}}{\Delta H_{des}}$	$\frac{C_{p,ref,liq} \Delta T_L}{L_{evap}}$	DTMR
Combined condenser/ evaporator cycle	CCE	$\frac{L_{evap}}{\Delta H_{des}}$	DTMR _E	DTMR _D
Resorption cycle	RES	$\frac{\Delta H_{LTS}}{\Delta H_{HTS}}$	DTMR _{LTR}	DTMR _{HTR}

$$Q_E = L_{evap}(1 - DTMR_E) \quad (11)$$

The desorber DTMR in Eq. (6) for conventional adsorption desorber or in Eq. (8) for ammoniate sorption desorber can be used for COP calculation for the combined condenser/evaporator cycle depending on the sorption process. The heating COP for this combined condenser/evaporator cycle is shown in Eq. (12).

$$COP_{ht} = 1 + \frac{L_{evap}(1 - DTMR_E)}{L_{des}(1 + DTMR_D)} \quad (12)$$

2.4. COP expression for resorption cycle with two reactors and two adsorbents

For the resorption cycle with two reactors (a high temperature reactor (HTR) and a low temperature reactor (LTR) and two adsorbents (high/low temperature salt [HTS and LTS]), the cooling COP is defined as the heat absorbed by the LTR divided by heat required by the HTR. Correspondingly, heating COP is cooling COP plus one. Like the combined condenser/evaporator cycle, DTMR should be considered in both reactors. Eqs. (13) and (14) illustrate the DTMR for low and high temperature reactors. The heating COP is expressed in Eq. (15). The temperature lift ΔT_L is defined as the difference between the adsorption and desorption temperature of LTS ($T_{ads, LTS} - T_{des, LTS}$); the temperature difference ΔT_D is defined as the difference between the desorption and adsorption temperature of HTS ($T_{des, HTS} - T_{ads, HTS}$). When there are multiple steps of reactions for LTS or HTS, the COP should combine all the reactions together as shown in Eq. (16).

$$DTMR_{LTR} = \frac{\Delta T_L}{\Delta Y_{HTS} m_{HTS} \Delta H_{LTS}} (\rho_{HTF, LTR} V_{HTF, LTR} C_{p, HTF, LTR} + \rho_{mat, LTR} V_{mat, LTR} C_{p, mat, LTR} + (1 + Y_{max, LTS}) m_{LTS} C_{p, LTS, comp}) \quad (13)$$

$$DTMR_{HTR} = \frac{\Delta T_D}{\Delta Y_{HTS} m_{HTS} \Delta H_{HTS}} (\rho_{HTF, HTR} V_{HTF, HTR} C_{p, HTF, HTR} + \rho_{mat, HTR} V_{mat, HTR} C_{p, mat, HTR} + (1 + Y_{max, HTS}) m_{HTS} C_{p, HTS, comp}) \quad (14)$$

$$COP_{ht} = 1 + \frac{\Delta H_{LTS}(1 - DTMR_{LTR})}{\Delta H_{HTS}(1 + DTMR_{HTR})} \quad (15)$$

$$COP_{ht} = 1 + \frac{\sum_{i=1}^n \frac{\Delta Y_{LTS,i} \Delta H_{LTS,i}}{\Delta Y_{LTS}} (1 - DTMR_{LTR})}{\sum_{j=1}^m \frac{\Delta Y_{HTS,j} \Delta H_{HTS,j}}{\Delta Y_{HTS}} (1 + DTMR_{HTR})} \quad (16)$$

2.5. Unified expression for all configuration types

Based on Eqs. (1), (5), (7), (9), (12), and (15) or (16), the universal expression of heating COP for a sorption system is shown in Eq. (17), and the meaning of each term is explained in Table 1. The systems related to ammoniate sorption are SCE, CCE, and RES.

$$COP_{ht} = 1 + \psi \frac{1 - \theta_1}{1 + \theta_2} \quad (17)$$

Fig. 2. System with heat recovery (using a combined condenser/evaporator as an example).

Any one of these configurations is generally capable of incorporating heat recovery, according to the following considerations.

Heat recovery can be accomplished from the ΔT_L -coupled heat exchange process, where at least two discrete heat exchangers are used for heat exchange with T_{cond} and T_{evap} . The fraction of sensible heat recovered from the ΔT_L -coupled heat exchangers is denoted here as ε_1 , as shown in Fig. 2.

Similarly, any one of these configurations is capable of incorporating heat recovery from the ΔT_D -coupled heat exchange process, when at least two discrete heat exchangers are used for heat exchange with T_{des} and T_{ads} . The fraction of sensible heat recovered from the ΔT_D -coupled heat exchangers is denoted here as ε_2 , as also shown in Fig. 2.

To accommodate heat recovery, Eq. (17), which assumes no heat recovery, can be modified as shown in Eq. (18). Note that heat recovery ε_1 is always zero for cycles not considering dead thermal mass in the low temperature heat source-driven reactor.

Note that the effectivenesses ε_1 and ε_2 act only on the sensible heat. This can be observed by inspection of Eq. (18) and the definition of θ_1 and θ_2 , by evaluating these expressions with values of $\varepsilon_1 = \varepsilon_2 = 0$ and $\varepsilon_1 = \varepsilon_2 = 1$. In other words, in this work, heat recovery effectiveness is the fraction of sensible heat that can be recovered. A scheme that recovers latent heat as well (such as the well-known generator-absorber exchange or GAX cycle) would have an effectiveness greater than one since latent heat is recovered in addition to sensible heat.

$$COP_{ht} = 1 + \psi \frac{1 - (1 - \varepsilon_1)\theta_1}{1 + (1 - \varepsilon_2)\theta_2} \quad (18)$$

In Eqs. (17) and (18), the ratio expression after ψ shows the gap between real cooling COP and maximum single effect cooling COP because of the effects of dead thermal mass and other penalties. We name this ratio as the COP approach factor (λ), as shown in Eq. (19). A higher λ means the COP is closer to maximum COP.

Table 2Comparison of DTM_{design} and $DTM_{inherent}$ for each configuration and heat exchanger type.

Type ^a	DTM_{design}	$DTM_{inherent}$
ABS	0	$(1 - \varepsilon_{SHX})(1 + Y_{max})m_{abs}C_{p,sol}$
ADS	$\rho_{HTF}V_{HTF}C_{p,HTF} + \rho_{mat}V_{mat}C_{p,mat}$	$m_{ads}(C_{p,ads} + Y_{max}C_{p,ref,liq})$
SCE	$\rho_{HTF}V_{HTF}C_{p,HTF} + \rho_{mat}V_{mat}C_{p,mat}$	$(1 + Y_{max})m_{ads}C_{p,comp}$
CCE—Evaporator	$\rho_{HTF}V_{HTF}C_{p,HTF} + \rho_{mat}V_{mat}C_{p,mat}$	$m_{ref,ref}C_{p,ref,liq}$
CCE—Desorber	$\rho_{HTF}V_{HTF}C_{p,HTF} + \rho_{mat}V_{mat}C_{p,mat}$	$(1 + Y_{max})m_{ads}C_{p,comp}$
RES—LTR	$\rho_{HTF}V_{HTF}C_{p,HTF} + \rho_{mat}V_{mat}C_{p,mat}$	$(1 + Y_{max,LTS})m_{LTS}C_{p,LTS,comp}$
RES—HTR	$\rho_{HTF}V_{HTF}C_{p,HTF} + \rho_{mat}V_{mat}C_{p,mat}$	$(1 + Y_{max,HTS})m_{HTS}C_{p,HTS,comp}$

^a ABS = absorption cycle; ADS = adsorption cycle; DTM = dead thermal mass; SCE = separate condenser and evaporator; CCE = combined condenser/evaporator; RES = resorption cycle; LTR = low temperature reactor; HTR = high temperature reactor.

When λ equals 1, the real COP is equal to maximum COP.

$$\lambda = \frac{1 - (1 - \varepsilon_1)\theta_1}{1 + (1 - \varepsilon_2)\theta_2} \quad (19)$$

Combining this definition with Eq. (18) yields Eq. (20).

$$COP_{ht} = 1 + \psi\lambda \quad (20)$$

In Eqs. (6), (8), (10), (13), and (14), the DTM can be defined as the sum of two parts as shown in Eq. (21). For each heat exchanger type, the definitions of DTM_{design} and $DTM_{inherent}$ change slightly, as shown in Table 2.

$$DTM = DTM_{design} + DTM_{inherent} \quad (21)$$

The DTM_{design} represents the dead thermal mass of HTF and heat exchanger material. Clearly, this has a very strong dependence on reactor dimensions and design. This is generally the primary source of dead thermal mass, and it can be optimized.

The $DTM_{inherent}$ represents the dead thermal mass of salt and refrigerant. These depend primarily on inherent thermophysical properties. However, it is also important to note that, since the quantity of refrigerant may vary with cycle time and other operating conditions, the $DTM_{inherent}$ does have some slight dependence on operating conditions.

For reactor design, the ideal condition is when DTM_{design} equals zero. With a given working pair, working condition, mass of salt, and mass of refrigerant vapor, a better design usually means a lower DTM_{design} and higher performance.

3. Model verification and validation

In this section, we focus on the cooling COP because it is the most widely available in existing literature. The heating COP model is considered verified and validated at the same time because of its connection with cooling COP (as expressed in Eq. (1)).

Most published literature on experimental and modeled performance of sorption systems does not include sufficient information to determine the dead thermal mass of the system in question. A few examples were found. For all of these examples that included sufficient information about dead thermal mass, we performed validation against experimental studies and verification with numerical studies, as described in Sections 3.1 and 3.2.

3.1. Conventional absorption and adsorption cycles

For conventional absorption and adsorption cycles, the COP expression used in this work is identical to those used by two previous references, as follows.

The COP expression for a conventional absorption heat pump was verified previously by Gluesenkamp (2012) by comparing the analytical model of cooling COP with the result from a numerical model for single effect absorption chiller in Herold et al. (2016). The analytical model COP was 0.735, and the COP from the detailed numerical model was 0.720.

Table 3Parameters used in coefficient of performance verification^a.

	Value	Unit
$T_{des, HTS}$	150	°C
$T_{ads, HTS}$	30	°C
$T_{des, LTS}$	5	°C
$T_{ads, LTS}$	30	°C
ΔT_D	120	K
ΔT_L	25	K
Properties of reactors	HTS	LTS
Mass of salt	2.57	2.125 kg
Mass of expanded graphite	1.385	1.145 kg
Mass of heat exchange material	15	12 kg
Volume of HTF	9	7.8 L
Density of HTF	N/A ^b	N/A ^b kg L ⁻¹
Specific heat of HTF	N/A ^b	N/A ^b kJ kg ⁻¹ K ⁻¹
Specific heat of salt ^b	0.6	0.44 kJ kg ⁻¹ K ⁻¹
Specific heat of expanded graphite ^c	0.61	0.61 kJ kg ⁻¹ K ⁻¹
Specific heat of liquid refrigerant ^c	4.59	4.59 kJ kg ⁻¹ K ⁻¹
Specific heat of stainless steel ^c	0.46	0.46 kJ kg ⁻¹ K ⁻¹
Maximum loading	0.486	0.710 kg ⁻¹ salt
Differential loading	0.432	– kg ⁻¹ salt
Reaction heat ^d	2789	2250 kJ kg ⁻¹ ref

Notes: HTS = high temperature salt; LTS = low temperature salt; HTF = heat transfer fluid.

^a Source: Lepinasse et al. (1994). Modelling and experimental investigation of a new type of thermochemical transformer based on the coupling of two solid–gas reactions. *Chemical Engineering and Processing: Process Intensification*, 33 (3), 125–134.

^b Values were not provided in the original source.

^c Specific heat comes from: Bao et al. (2011). Working pairs for resorption refrigerator. *Applied Thermal Engineering*, 31 (14), 3015–3021.

^d Reaction heat comes from: Li et al. (2014). Progress in the development of solid–gas sorption refrigeration thermodynamic cycle driven by low-grade thermal energy. *Progress in Energy and Combustion Science*, 40, 1–58.

The COP expression for a conventional adsorption heat pump was verified previously by Qian et al. (2013). The cooling COP analytical model was compared with experiment data of 170 test points for a synthetic zeolite-based adsorption system. The difference was within a $\pm 10\%$ range.

3.2. Resorption cycle with two reactors and two adsorbents

Two sources, both using ammoniate sorption, were used to confirm the analytical model for the resorption cycle with two reactors and two adsorbents. The sensible heat of both reactors was considered.

The analytical model in this work was verified against the numerical model for the resorption cycle using two solid–gas reactors studied by Lepinasse et al. (1994). $MnCl_2$ and $BaCl_2$ were used as HTS and LTS, respectively. Lepinasse et al. (1994) validated their numerical model against experimental results. The input parameters for the model calculation are shown in Table 3.

Table 4

Comparison of coefficient of performance (COP) calculation result between analytical and numerical models.

	With dead thermal mass of adsorbent	With dead thermal mass of adsorbent + heat exchange material
$DTMR_{HTR}$	0.31	0.58
$DTMR_{LTR}$	0.09	0.14
$COP_{analytical}$ (this work)	0.56	0.44
$COP_{numerical}^a$	0.54	0.45

Note: DTMR = dead thermal mass ratio; LTR = low temperature reactor; HTR = high temperature reactor.

^a Lepinasse et al. (1994). Modelling and experimental investigation of a new type of thermochemical transformer based on the coupling of two solid-gas reactions. *Chemical Engineering and Processing: Process Intensification* 33 (3), 125–134.**Table 5**Parameters used in coefficient of performance validation^a.

		Working pair			
		MnCl ₂ /NH ₄ Cl	MnCl ₂ /NaBr		
ΔT_D	K	65		120	
ΔT_L	K	30		30	
		HTS	LTS	HTS	LTS
Mass of salt	g	100.09	55.35	55.5	34.59
Mass of expanded graphite	g	50.06	27.51	29.88	18.63
Mass of heat exchange material	g	774.38	582.89	732.42	515.98
Specific heat of salt	kJ kg ⁻¹ K ⁻¹	0.61	1.55	0.6	0.505
Specific heat of expanded graphite	kJ kg ⁻¹ K ⁻¹	0.61	0.61	0.61	0.61
Specific heat of refrigerant	kJ kg ⁻¹ K ⁻¹	4.59	4.59	4.59	4.59
Specific heat of stainless steel	kJ kg ⁻¹ K ⁻¹	0.46	0.46	0.46	0.46
Maximum loading	kg ⁻¹ _{salt}	0.486	0.812	0.518	0.781
Differential loading	kg ⁻¹ _{salt}	0.432	–	0.507	–
Reaction heat	kJ kg ⁻¹ _{ref}	2740	1630	2924	1790

Notes: HTS = high temperature salt; LTS = low temperature salt.

^a Source: Xu et al., (2011). Resorption system with simultaneous heat and cold production. *International Journal of Refrigeration* 34 (5), 1262–1267.**Table 6**

Comparison of coefficient of performance (COP) between analytical model and experiment result.

	Working pair	
	MnCl ₂ /NH ₄ Cl	MnCl ₂ /NaBr
$DTMR_{HTR}$	0.368	0.759
$DTMR_{LTR}$	0.246	0.232
$COP_{analytical}$ (this work)	0.33	0.27
$COP_{experiment}^a$	0.35	0.31

Notes: DTMR = dead thermal mass ratio; LTR = low temperature reactor; HTR = high temperature reactor.

^a Source: Xu et al., (2011). Resorption system with simultaneous heat and cold production. *International Journal of Refrigeration* 34 (5), 1262–1267.

less than 0.04. Therefore, the analytical model demonstrates a good agreement with experimental result.

In this section, the analytical model of cooling COP was verified against numerical model results in the literature and was validated against experimental results in the literature. The maximum cooling COP deviation was less than 0.04. Based on Eq. (1), the heating COP model was also verified and validated, and the relative difference in COP would be lower for heating COP.

4. Using the model to choose the best cycle for an example application

In this section, the verified analytical model is used to evaluate and determine the optimal cycle configuration and working pairs for a sorption heat pump used in a space heating application. In this example application, the assumed design target of the sorption heat pump for space heating is to produce 10 kW of 50 °C hot water at an ambient of –10 °C and with a heat source temperature of 250 °C.

4.1. Selection of working pair

To select optimal working pairs for the sorption heat pump, equilibrium lines of potential ammoniates are illustrated on a Clapeyron diagram in Fig. 3. The operating temperatures and pressures are also shown in Fig. 3. The choices of LTS shown in the blue area on Fig. 3 are constrained by the ambient temperature. However, the operating pressure should also be considered, as in practice high vacuum conditions (i.e., low ammonia vapor pressures) usually lead to a limited mass transfer rate and subsequently low heating power. Therefore, the LTSs operating at higher pressure (lighter blue area) are better options than those that operate at low pressure (darker blue area). The choices of HTS are shown in the red area of Fig. 3. In the case of the HTS selection, the con-

Fig. 3. The Clapeyron diagram of different reaction steps. [Notes: 0-NH₃; 1-NH₄Cl (3/0); 2-PbCl₂ (8/3.25); 3-NaBr (5.25/0); 4-BaCl₂ (8/0); 5-LiCl (4/3); 6-PbCl₂ (3.25/2); 7-CaCl₂ (8/4); 8-CaCl₂ (4/2); 9-LiCl (3/2); 10-LiCl (2/1); 11-MnCl₂ (6/2); 12-LiCl (1/0); 13-MgCl₂ (6/2); 14-NiCl₂ (6/2). ①—ambient temperature; ②—hot water supply temperature; ③—heat source temperature; ④—assumed highest feasible pressure; ⑤—assumed lowest feasible pressure. Reaction enthalpy and entropy come from Li et al. (2014)].

Table 7

Heating coefficient of performance and sorbent mass for different working pairs.

Resorption		ψ	Sorbent mass [g kJ ⁻¹]	
HTS	LTS		HTS	LTS
MnCl ₂ (6/2)	NH ₄ Cl (3/0)	1.62	0.66	0.60
LiCl (3/0)	NH ₄ Cl (3/0)	1.61	0.29	0.60
MgCl ₂ (6/2)	NH ₄ Cl (3/0)	1.53	0.43	0.60
MnCl ₂ (6/2)	PbCl ₂ (8/3.25)	1.72	0.66	1.71
LiCl (3/0)	PbCl ₂ (8/3.25)	1.71	0.29	1.71
MgCl ₂ (6/2)	PbCl ₂ (8/3.25)	1.62	0.43	1.71
MnCl ₂ (6/2)	NaBr (5.25/0)	1.75	0.66	0.55
LiCl (3/0)	NaBr (5.25/0)	1.73	0.29	0.55
MgCl ₂ (6/2)	NaBr (5.25/0)	1.64	0.43	0.55
MnCl ₂ (6/2)	BaCl ₂ (8/0)	1.81	0.66	0.68
LiCl (3/0)	BaCl ₂ (8/0)	1.79	0.29	0.68
MgCl ₂ (6/2)	BaCl ₂ (8/0)	1.69	0.43	0.68
Sorption		ψ	Sorbent mass [g kJ⁻¹]	
MnCl ₂ (6/2)		1.43	0.66	
LiCl (3/0)		1.42	0.29	
MgCl ₂ (6/2)		1.37	0.43	

Notes: HTS = high temperature salt; LTS = low temperature salt.

highest ψ (see Table 7); however, the extremely low operating pressure of BaCl₂ as the LTS is a major concern because of low power density. In practice, lower power density tends toward a larger (and thus more expensive) system for a given heating capacity. NaBr and PbCl₂ as LTS have similar ψ and higher operating pressure, but PbCl₂ has much lower energy density (Li et al., 2013) manifested as an elevated sorbent mass per unit of reaction heat in one desorption or sorption mode (g kJ). As shown in Table 7, using MnCl₂ or LiCl as the HTS leads to higher COPs compared with using MgCl₂ as the HTS. However, again LiCl has higher energy density and lower sorbent mass per unit of reaction heat than that of MnCl₂.

The best candidates for the resorption cycle are NaBr (5.25/0) as LTS and LiCl (3/0) as HTS because this working pair has demonstrated a good ψ and a low sorbent mass per unit of refrigerant latent heat. Correspondingly, in the case of the SCE and CCE sorption cycles, LiCl as HTS is considered the best option.

4.2. Selection of system configuration

The aim of this section is to find a suitable system configuration to realize a higher COP more easily. This is determined by both ψ (defined in Section 4.1) and the COP approach factor λ (defined in Eq. (20)).

We defined DTM as the sum of design-related DTM_{design} and fluid-related $DTM_{inherent}$ (see Eq. (21)). In Fig. 5, the effect of DTM_{design} on θ_1 , θ_2 , and λ for each working pair and configuration is illustrated. Generally systems are easier to build with a higher allowance for DTM_{design} , but the performance is limited; with low DTM_{design} and higher theoretical performance, realizing the design becomes increasingly challenging. We plot the figure applying LiCl/NaBr for RES cycle and LiCl for SCE and CCE cycles to illustrate the main trends. We also plot two of the most commonly used working pairs for RES as reference of how much the DTM_{design} and λ can be in common practice; oil is assumed to be the HTF with density of 890 (kg m⁻³) and specific heat of 1.8 (kJ kg⁻¹ K⁻¹).

To make the DTM_{design} for different applications comparable, we use the ratio of DTM_{design} divided by active mass of refrigerant ($\Delta Y m_{ads}$) to represent DTM_{design} level of one application. The active mass of refrigerant means the total mass of refrigerant vapor adsorbed for heating in sorption mode. For simplicity, we assume that DTM_{design} of LTR equals DTM_{design} of HTR for the RES configuration and that DTM_{design} of the salt reactor is twice the DTM_{design} of the C/E for the CCE cycle. These assumptions are deemed reasonable for the authors' current application but might be different for other exchanger design and heat transfer fluid flow network design. With the present model the system designer can change relation between DTM_{design} of HTR, LTR, and C/E according to their own design level and draw a similar figure for comparison.

According to Fig. 4, the SCE and CCE cycles using LiCl salt have the same θ_1 , θ_2 , and λ when $DTM_{design} = 0$. As the DTM_{design} level increases, the CCE has a lower λ than SCE cycle. The λ difference between the CCE and SCE cycles increases because the CCE cycle has to consider the DTM_{design} of C/E HTF and materials. Comparing λ of SCE using LiCl and RES using LiCl/NaBr, the λ of the RES cycle is higher than that of the SCE cycle when the DTM_{design} level is low; the λ of the SCE cycle is higher than that of the RES cycle when the DTM_{design} level is high. Given reactor design properties like mass of HTF and mass of material, the DTM_{design} level can be calculated, and the performance of different cycles can be compared easily. For example, the DTM_{design} levels of design calculated according to Table 8 for SCE, CCE, and RES configurations are shown as black "X" mark points in Fig. 5. The SCE cycle has slightly better λ than the RES cycle. However, the difference of λ is small so that the RES cycle using LiCl/NaBr may still have higher

Fig. 4. Effect of dead thermal mass (DTM), θ_1 , and θ_2 on λ . The relative dead thermal mass of the low-temperature-coupled component(s) are denoted θ_1 ; and θ_2 for the high-temperature coupled components. These combine to form the penalty factor λ as defined in Eq. (19).

Table 8
Comparison of different system configurations.

Configuration	Working pair	ψ	θ_1	θ_2	$COP_{ht}, \varepsilon_1 = \varepsilon_2 = 0$	$COP_{ht}, \varepsilon_1 = \varepsilon_2 = 0.5$
SCE	LiCl (3/0)	0.42	0.27	0.48	1.21	1.29
CCE	LiCl (3/0)	0.42	0.44	0.48	1.16	1.27
RES	LiCl/NaBr	0.73	0.32	0.48	1.34	1.50

Notes: COP = coefficient of performance; SCE = separate condenser and evaporator; CCE = combined condenser/evaporator; RES = resorption cycle.

Fig. 5. Contribution of each dead thermal mass factor to DTMR for the LiCl/NaBr RES and CCE cycles (Notes: HTF = heat transfer fluid; C/E = condenser/evaporator; DTMR = dead thermal mass ratio; RES = resorption cycle; CCE = combined condenser evaporator cycle).

($\varepsilon_1 = \varepsilon_2 = 0$) and with 50% heat recovery were considered. Since heat recovery in this work only involves sensible heat recovery, a value of 50% corresponds to equilibration of the temperatures of two relevant heat exchangers before switching phases, and thus represents an upper limit for many systems.

The LiCl/NaBr resorption cycle has the highest heating COP of 1.34 without sensible heat recovery. And this number can be improved to 1.50 when 50% sensible heat recovery is applied.

This section illustrated the use of the analytical model in the selection of working pairs and configurations, the analysis of each dead thermal mass factor effect on performance, and the influence of working condition on performance. The analytical model is also applied to study the effect of reactor design on performance for each configuration and the effect of sensible heat recovery on performance.

5. Discussion

5.1. Dead thermal mass

In this section, the influence of dead thermal mass ratio DTMR on the performance of the sorption and resorption cycles is discussed for the working pairs selected in Section 4.1. Note that the

Table 9

Dead mass for LiCl/NaBr reactor and condenser/evaporator (C/E) reactor.

		LiCl	NaBr	C/E
Mass of heat transfer fluid	kg	15.1	15.1	7.9
Mass of salt	kg	20.7	43.8	–
Mass of heat exchange material	kg	60	60	27

reactors, the main contribution comes from HTF; for C/E reactors, the main contribution comes from retained refrigerant.

The model was also applied to predict the performance change under different working conditions. The heating COP of the RES, CCE, and SCE cycles increases from 1.31 to 1.37, 1.14 to 1.19, and 1.19 to 1.22, respectively, when the ambient temperature rises from -23°C to 5°C .

The comparison of different system configurations applying selected working pairs was carried out using the analytical model. The effect of dead thermal mass of HTF and reactor material on λ was studied. The CCE cycle has lower λ than the other two cycles. In a practical range of DTM_{design} , LiCl/NaBr RES cycle and LiCl SCE cycles have very similar λ . Therefore, the LiCl/NaBr RES cycle will have better COP because of the benefit of higher ψ .

Based on a simple analytical model calculation, for space heating applications at ambient temperature -10°C , heat delivery temperature of 50°C and up to 250°C driving heat source temperature, without heat recovery the highest efficiency is obtained with the LiCl/NaBr resorption cycle, with a COP 11–15% higher than that of the competing options. With 50% recovery of sensible heat, LiCl/NaBr still has the highest COP, 16–18% higher than that of the competing options. The LiCl/NaBr RES cycle is shown to be a good option for the sorption cycle in space heating applications.

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salt LiCl will go through three reaction steps: 3/2, 2/1, and 1/0. In this work, the dead masses shown in Table 9 are assumed for each component. Based on personal experience of the authors in development of the system described in Blackman et al. (2017), these masses are considered reasonable for a system producing 10 kW of 50°C hot water at an ambient of -10°C and with a heat source temperature of 250°C .

The contribution of each component of dead thermal mass to the DTMR of each reactor is calculated based on the geometry of the novel sorption heat pump reactor; the results are shown in Fig. 5. In the resorption cycle with the LiCl reactor and NaBr reactor, the dead thermal mass of HTF contributes to almost half of the DTMR; in the CCE sorption cycle, DTMR of the C/E reactor is influenced mainly by the retained refrigerant at the end of the condensation process. In the sorption cycle with separate condenser and evaporator (SCE), the DTMR of condenser and evaporator is zero.

5.2. Model response to working temperatures

As ambient temperature changes from the design point temperature, the temperature lift ΔT_L (i.e., $T_{cond} - T_{evap}$) is influenced more than the temperature difference ΔT_D (i.e., $T_{des} - T_{abs}$); therefore, the DTMR of a LiCl reactor (HTS) remains almost the same. However, the DTMR of a NaBr reactor (LTS) and C/E are reduced for higher ambient temperature and increased for lower ambient temperature; therefore, the heating COP increases at temperatures higher than design point and decreases at lower temperatures. For simplicity, we assume that differential loading ΔY is constant. In reality, this would require varying cycle time, with complex impacts on cycle power and ΔY , however such an analysis is beyond the scope of the present study. A wider temperature range is considered here to predict cycle performance under extreme cold and warmer condition. As evaluated using Eq. (20), the heating COP of the RES, CCE, and SCE cycles increases from 1.31 to 1.37, 1.14 to 1.19, and 1.19 to 1.22, respectively, when the ambient temperature rises from -23°C to 5°C .

6. Conclusion

In this study, a unified analytical model to calculate heating COP and enable rapid comparison of five different sorption cycles (ABS, ADS, SCE, CCE, and RES) was derived. This conceptual model allows direct comparison of diverse cycle types. The term DTMR was used to describe the effect of dead thermal mass on COP. The COP approach factor λ was defined based on the dead thermal mass for ammoniate sorption with separate condenser/evaporator, combined condenser/evaporator, and resorption cycles to allow direct comparison among these cycle types.

Using available numerical and experimental results in the literature, the analytical model was verified by a classical numerical model and validated by experiment results. The model was used along with a Clapeyron diagram to select a suitable working pair for an ammoniate sorption heat pump for space heating. LiCl/ NH_3 was selected for the RES cycle, and LiCl was selected for the SCE and CCE cycles.

The contribution of different dead thermal mass factors to the DTMR was studied based on the working pair selection. For salt

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