Comparative investigations of sorption/resorption/cascading cycles for long-term thermal energy storage

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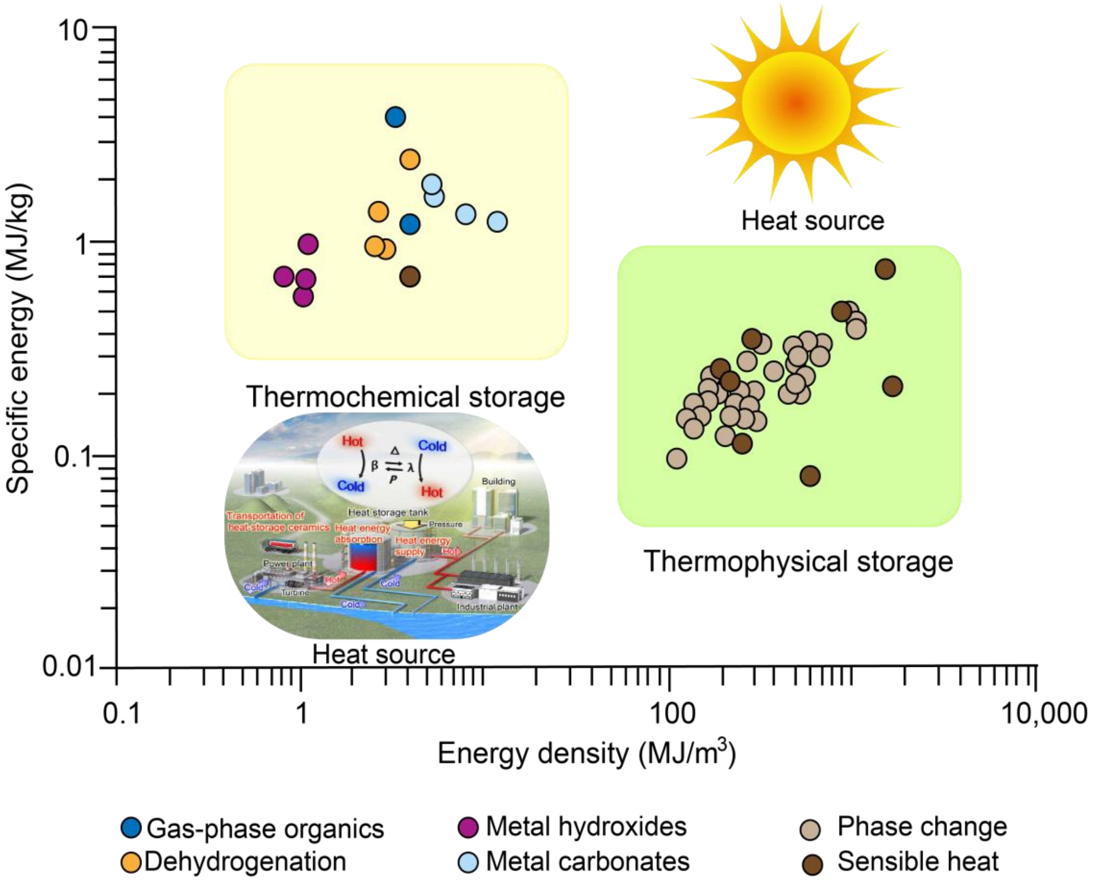
Shanghai

Contents

1. Background

> **Science** *‘More than 90% of the world’s primary energy generation is consumed or wasted thermally. Thermal energy storage has a broad and critical role to play in making energy use more sustainable for heating and cooling, solar energy harvesting, and other applications.’*

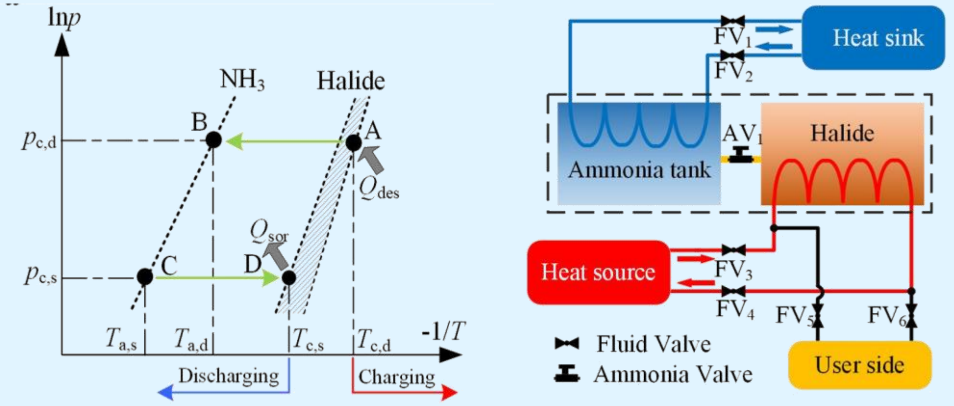


- ☐ Thermochemical storage owns higher specific energy density.
- ☐ Phase change storage possess constant heat storage grade.
- ☐ Thermochemical storage owns smaller heat loss.
- ☐ Sensible heat storage has strong adaptability to heat source.

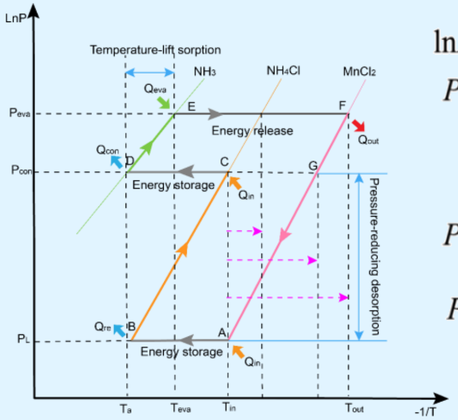
- ■ Research objective: delaying the decline of sorption heat storage grade and improving the adaptability of sorption heat storage to heat source.

Science, 2012; 335 (6075), 1454-1455. Sci. Adv. 2020; 6: 5264

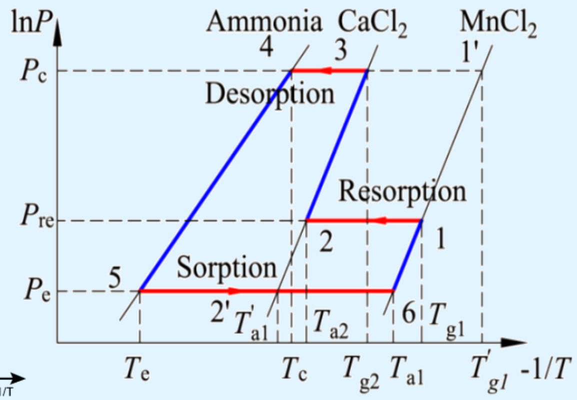
1. Background — research status



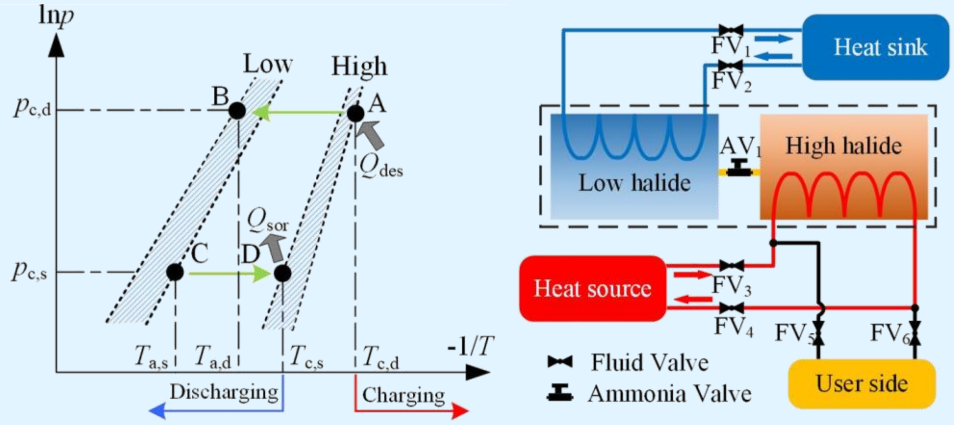
Single-stage sorption cycle



Two-stage grade promotion cycle



Two-stage sorption refrigeration cycle



Resorption cycle

- Industrial waste heat and solar energy **fluctuate greatly** under different time and weather conditions (**60~200^{o}C**).
- The **temperature fluctuation** of heat source will inevitably bring challenges to the **application reliability** of the sorption thermal storage system.

An et al. Energy, 2020; 212: 118756 Wu et al. Energy Convers. Manage. 2017; 148: 330

1 Background

2 **Materials and cycles**

3 Experimental test

4 Results and discussion

5 Conclusions

2. Materials and cycles — Materials selection

☐ Complexation reaction:

$$M_aX_b(NH_3)_n + (m-n)NH_3 \Leftrightarrow M_aX_b(NH_3)_m \qquad (1)$$

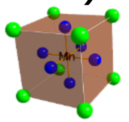
☐ Clapeyron equation:

$$T_{sta} = \Delta H / \left(\Delta S - R \cdot \ln p_{eq}\right) \qquad (2)$$

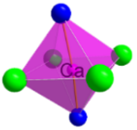
Table 1. Theoretical value of complexation reaction for halide-ammonia working pairs

NO.	Reaction	ΔH/ (J•mol^{-1})	ΔS/ (J•mol^{-1}•K^{-1})	T_{sta} (°C)	E_s (kJ•kg^{-1})
1	$PbCl_2(NH_3)_{8-3.25}$	34317	223.76	52.05	**586.12**
★ **2**	**$NH_4Cl(NH_3)_{3-0}$**	29433	207.90	55.10	**1650.8**
3	$BaCl_2(NH_3)_{8-0}$	37665	227.25	72.35	**1447.1**
4	$SnCl_2(NH_3)_{4-2.5}$	38920	229.82	75.64	**307.91**
5	$PbCl_2(NH_3)_{3.25-2}$	39339	230.27	77.98	**176.81**
★ **6**	**$CaCl_2(NH_3)_{8-4}$**	41013	230.30	92.82	**1477.9**
7	$SrCl_2(NH_3)_{8-1}$	41431	228.80	101.6	**1829.4**
★ **8**	**$CaCl_2(NH_3)_{4-2}$**	42268	229.92	105.3	**761.59**
9	$ZnCl_2(NH_3)_{6-4}$	44779	230.24	126.6	**657.07**
10	$PbCl_2(NH_3)_{2-1.5}$	46035	230.89	135.5	**82.764**
11	$PbCl_2(NH_3)_{1.5-1}$	47290	232.50	140.7	**85.020**
★ **12**	**$MnCl_2(NH_3)_{6-2}$**	47416	228.07	158.5	**1507.2**
13	$ZnCl_2(NH_3)_{4-2}$	49467	230.24	168.5	**725.85**
14	$CuCl_2(NH_3)_{5-3.3}$	50241	230.75	173.4	**635.73**
15	$FeCl_2(NH_3)_{6-2}$	51266	227.99	193.9	**1617.9**

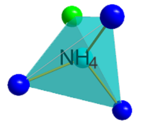
- High temperature halide (T_{sta}>150°C): $MnCl_2$;



- Middle temperature halide(90<T_{sta}< 150°C): $CaCl_2$;



- Low temperature halide (T_{sta}<90°C): NH_4Cl.



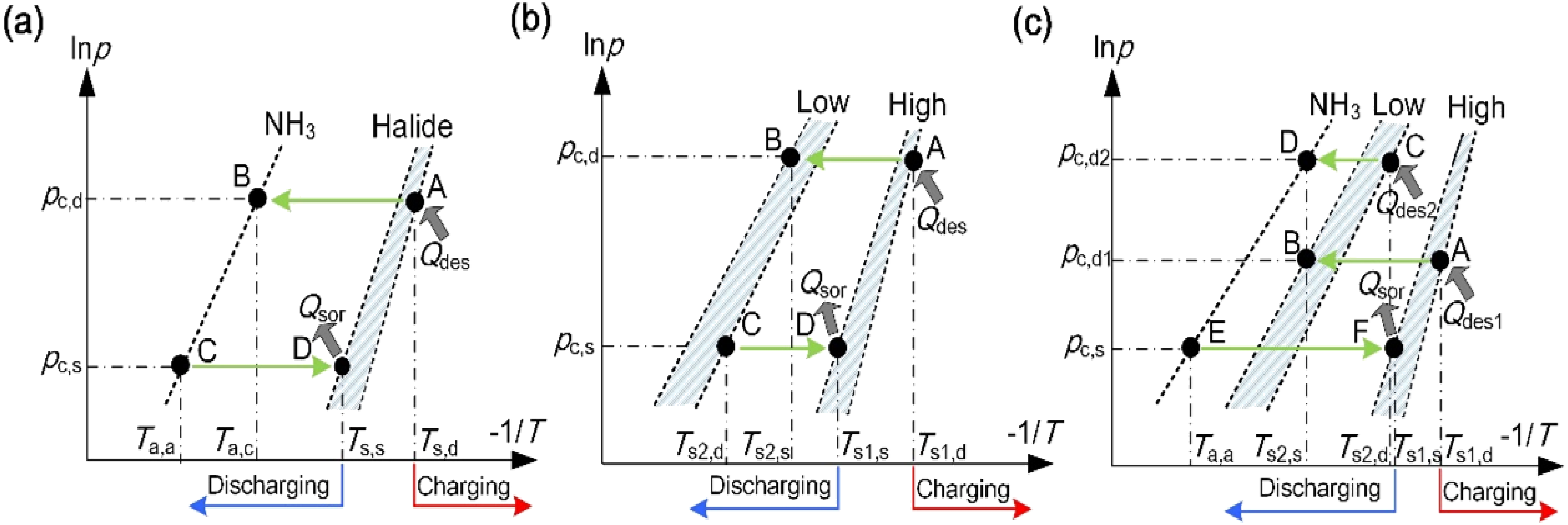
2. Materials and cycles — Cycles establishment

☐ Single-stage sorption cycle and resorption cycle (Fig. a~b):

For the heat charging process(A-B), $T_d > T_{s,d}$ or $T_{s1,d}$. For the heat discharging process(C-D), $T_s < T_{s,s}$ or $T_{s1,s}$, the heat output being transferred to the user side.

☐ Multi-stage cascading cycle (Fig. c):

Heat charging process includes the desorption stage of high-temperature halide (A-B), $T_d > T_{s1,d}$ and the desorption stage of low-temperature halide (C-D), $T_d > T_{s2,d}$. However, the heat discharging stage only involves high-temperature halide adsorbing ammonia (E-F) , $T_s < T_{s1,s}$.

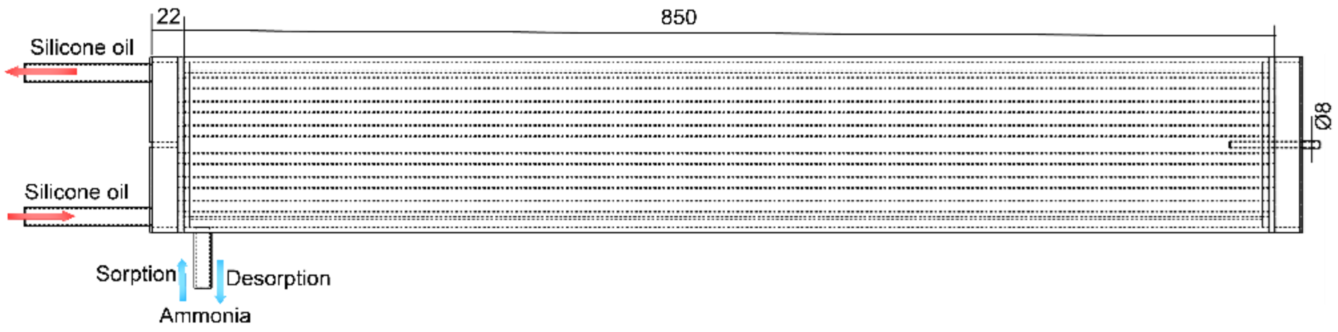


Working principles of (a) single-stage sorption, (b) resorption cycle and (c) multi-stage cascading cycle

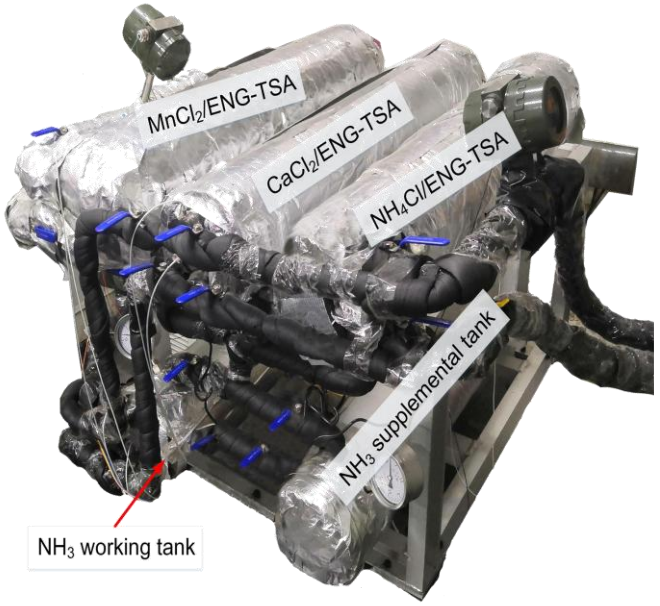
1. Background
2. Materials and cycles
3. **Experimental test**
4. Results and discussion
5. Conclusions

3. Experimental test — System construction

- The experimental system includes three temperature controllable sorption beds, a temperature controlable working ammonia tank, an ammonia supplemental tank, eight temperature measuring points, four pressure measuring points.
- During the sorption process, ammonia can enter the shell side of the sorption bed from the circular hole of the outer cylinder and it can be adsorbed by the sorbents after passing through the wire mesh and pore plate. Ammonia flows out in reverse during desorption process.



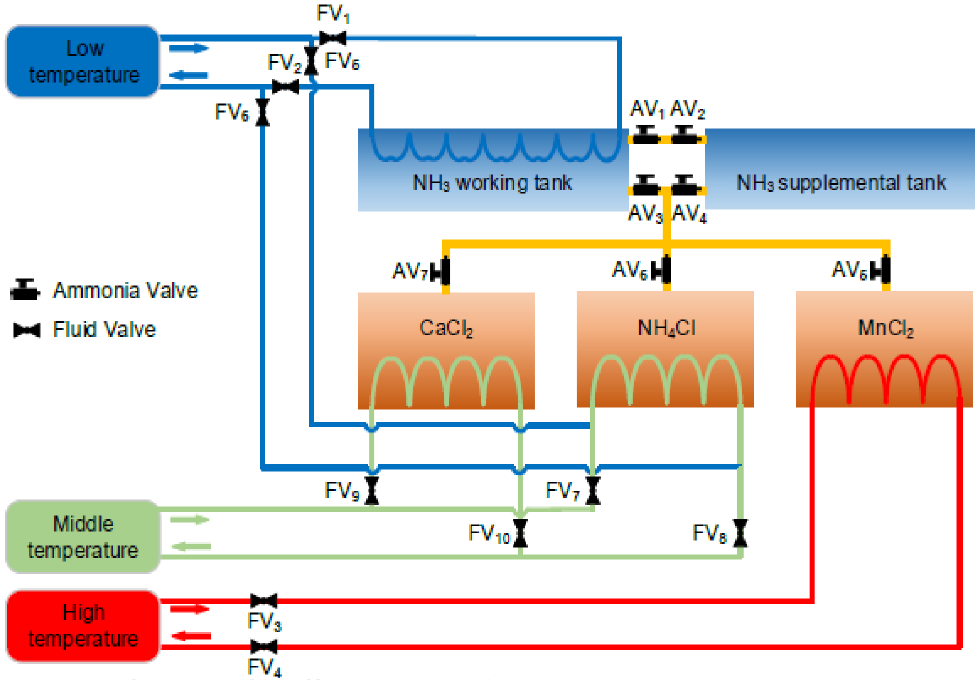
Structure diagram of sorption bed



Layout of overall test system

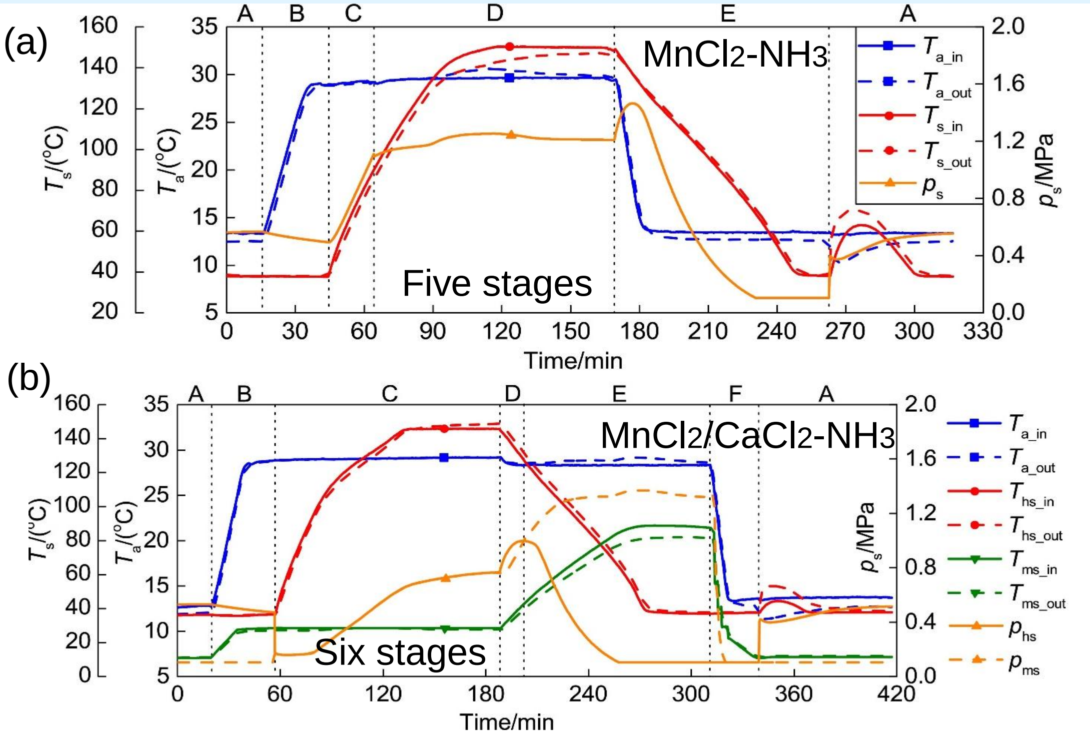
3. Experimental test — Working procedures

- ☐ Sorption/resorption cycles (Fig. a): (sorption stage A) AV3 and AV5 keep open; (switching stage B) AV3 or AV5 valves are closed; (preheating stage C) ammonia valves keep close; (desorption stage D) AV3 and AV5 keep open; (switching stage E) ammonia valves are closed.
- ☐ Multi-stage cascading cycle (Fig. b): (sorption stage A) AV3 and AV5 keep open; (switching stage B) AV3 or AV5 valves are closed; ($MnCl_2$ desorption stage C) AV5 and AV7 keep open; (preheating $CaCl_2$ stage D) ammonia valves closed; ($CaCl_2$ desorption stage E) AV3 and AV7 keep open; (switching stage F) ammonia valves are closed.



Schematic diagram of overall test system

Note: all valves are closed by default.



Working procedures

3. Experimental test — Performance evaluation

The input and output heat power of the sorption bed are expressed as Eqs. 3-4:

$$Q_{\mathrm{in}}' = Q_{\mathrm{in}} - Q_{\mathrm{loss}} = \dot{m}_{\mathrm{f}} c_{\mathrm{f}} (T_{\mathrm{f,in}} - T_{\mathrm{f,out}}) - (k_{\mathrm{loss}} T_{\mathrm{f,in}} + b_{\mathrm{loss}}) \quad (3)$$

$$Q_{\mathrm{out}}' = Q_{\mathrm{out}} + Q_{\mathrm{loss}} = \dot{m}_{\mathrm{f}} c_{\mathrm{f}} (T_{\mathrm{f,out}} - T_{\mathrm{f,in}}) + (k_{\mathrm{loss}} T_{\mathrm{f,in}} + b_{\mathrm{loss}}) \quad (4)$$

Thermal energy output density:

$$E_{\mathrm{out}} = \sum_{i=0}^{t_{\mathrm{dis}}} Q_{\mathrm{out}}'(t) / m_{\mathrm{sor,out}} \quad \text{(for single-stage sorption/resorption cyle)} \quad (5)$$

$$E_{\mathrm{out}} = \sum_{i=0}^{t_{\mathrm{dis}}} Q_{\mathrm{out}}'(t) / m_{\mathrm{sor,total}} \quad \text{(for multi-stage cascading cyle)} \quad (6)$$

Thermal energy storage efficiency: $\varepsilon = \sum_{i=0}^{t_{\mathrm{dis}}} Q_{\mathrm{out}}'(t) / \sum_{i=0}^{t_{\mathrm{cha}}} Q_{\mathrm{in}}'(t)$ (7)

Maximum temperature lift: $\Delta T_{\mathrm{max}}' = \mathrm{MAX}[Q_{\mathrm{out}}'(t) / (\dot{m}_{\mathrm{f}} c_{\mathrm{f}})]$ (8)

Effective discharging time: $t_{\mathrm{dis}} = t \quad (\text{if } Q_{\mathrm{out}}'(t) > 200\,\mathrm{W})$ (9)

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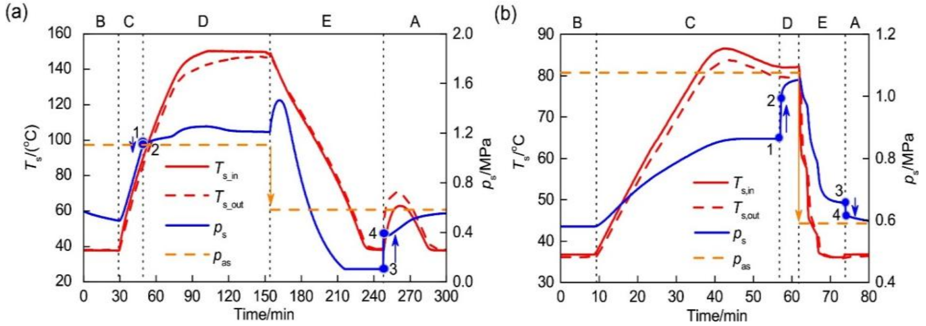
4. Results and discussion — Sorption cycle

4.1 The input and output heat power characteristics of various cycles



(a) $MnCl_2$-NH_3 cycle, (b) NH_4Cl-NH_3 cycle

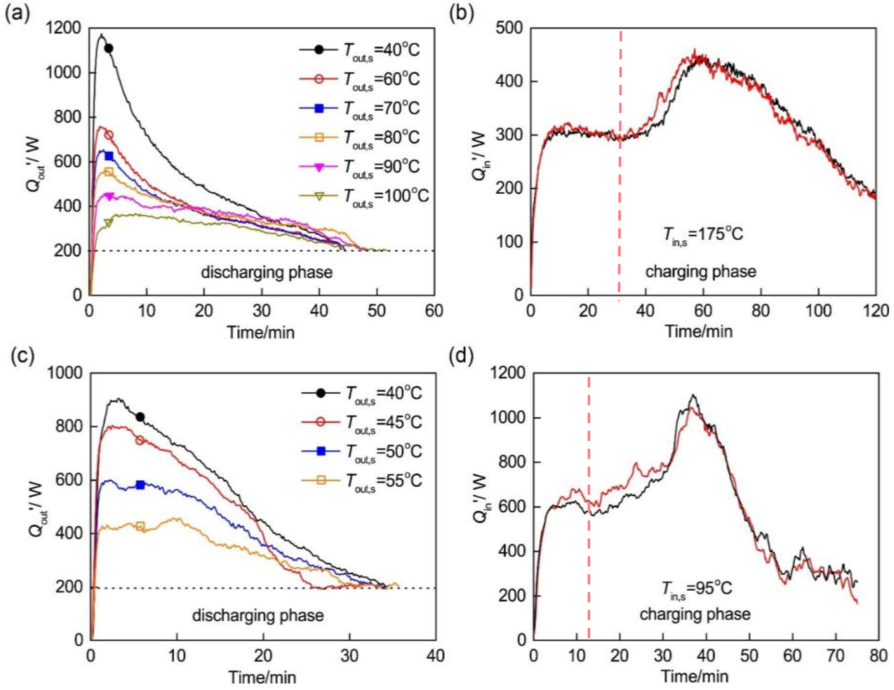
Point 1: $p_{bed}<p_{as}$, ammonia valve closed;

Point 2: $p_{sor}>p_{as}$, desorption reaction occurs;

Point 3: $p_{sor}>p_{as}$, ammonia valve closed；

Point 4: $p_{bed}<p_{as}$, sorption reaction happens.

■ NH_4Cl-NH_3 cycle is proved invalid.



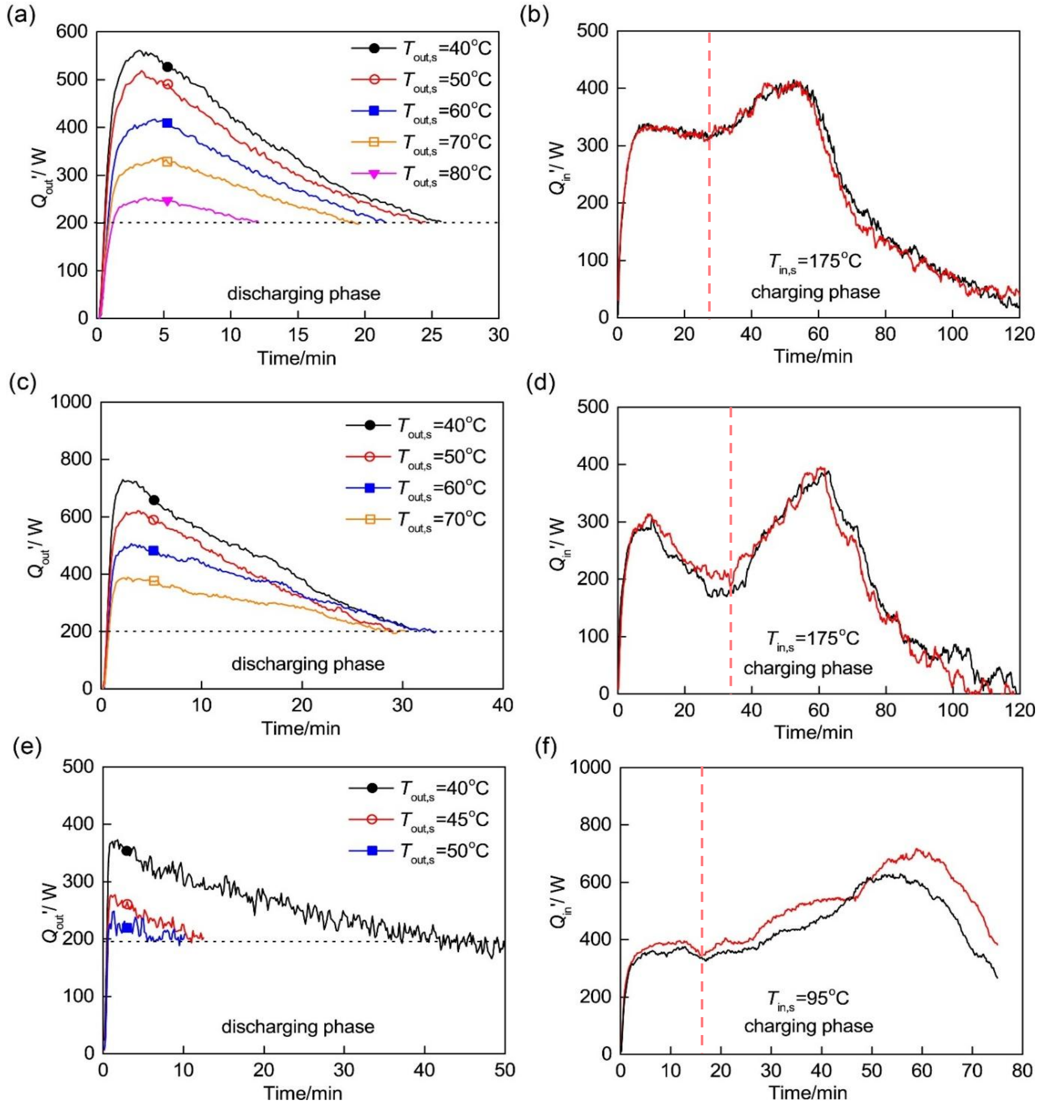
Output temperature & thermal storage power:
(a~b) $MnCl_2$-NH_3 cycle, (c~d) $CaCl_2$-NH_3 cycle

◆ The sorbents and the metal of sorption reactor are heated by sensible heat before opening the ammonia valve for desorption reaction.

◆ The maximum output power of $MnCl_2$-NH_3 and $CaCl_2$-NH_3 cycle with output temperature at 40°C can reach over 1100/900 W, while the maximum output power is lower than 400 W with output temperature at 100/55°C.

◆ The effective discharging time is over 40 min and 30 min.

4. Results and discussion — Resorption cycle



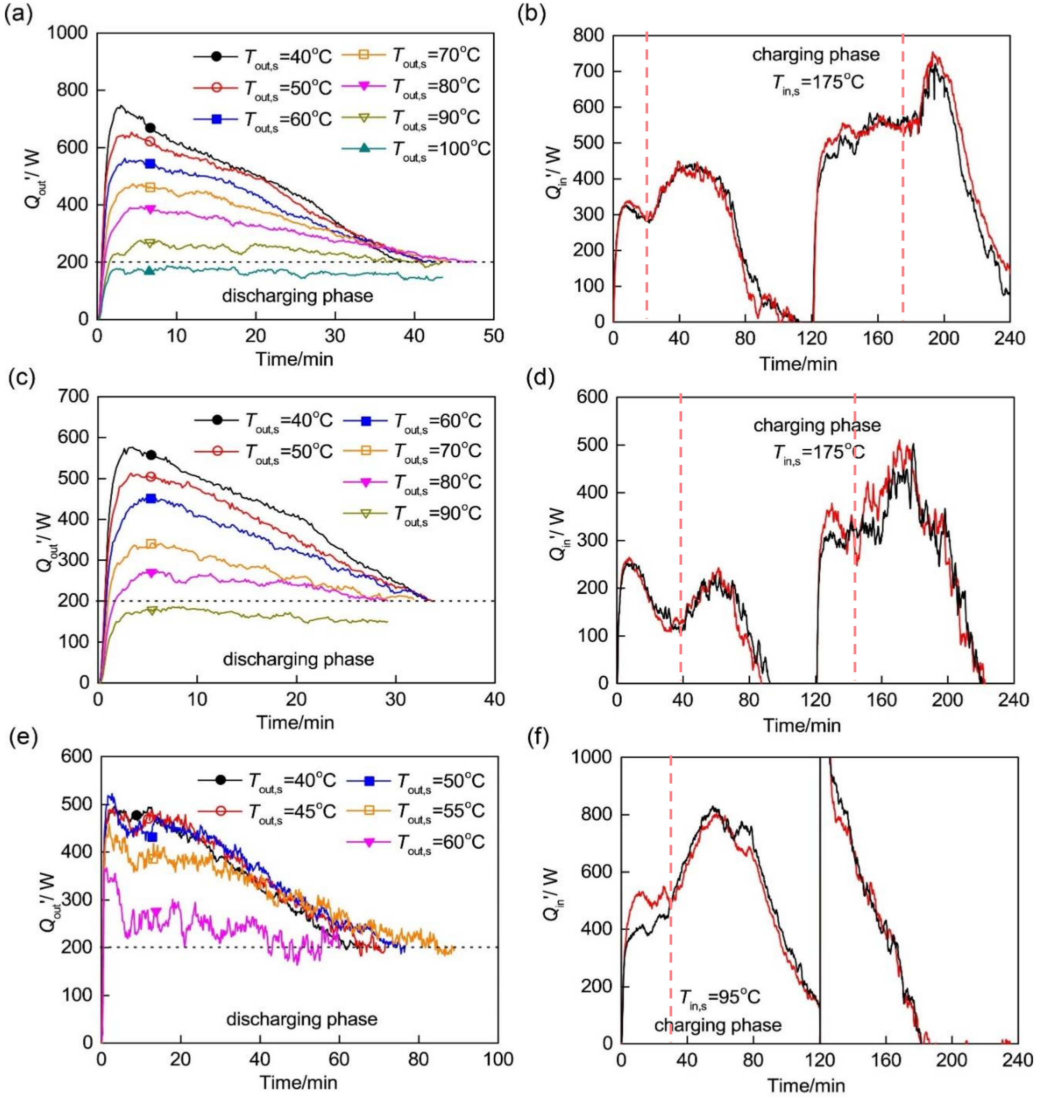
- Compared with single-stage sorption cycles, the maximum output power drops down dramatically lower than 600 W, 800 W and 400 W.

- The effective discharging time of $MnCl_2$-$CaCl_2$ cycle and $MnCl_2$-NH_4Cl cycle is much shorter than that of $MnCl_2$-NH_3 cycle.

- Especially for $CaCl_2$-NH_4Cl cycle, only 40°C is low enough to obtain proper output power and effective discharging time, otherwise the effective discharging time is limited to about 10 min.

Output temperature & thermal storage power: (a~b) output/input power of MnCl2-CaCl2 cycle, (c~d) MnCl2-NH4Cl cycle, (e~f) CaCl2-NH4Cl cycle

4. Results and discussion — Cascading cycle



Output temperature & thermal storage power: (a~b) output/input power of $MnCl_2/CaCl_2-NH_3$ cycle, (c~d) $MnCl_2/NH_4Cl-NH_3$ cycle, (e~f) $CaCl_2/NH_4Cl-NH_3$ cycle

◆ The charging phase is composed of two stages: resorption between halides and desorption of middle/low temperature halide.

◆ The maximum output power and effective discharging time of $MnCl_2/CaCl_2-NH_3$ cycle are around 700 W and 45 min, which are both greater than those of $MnCl_2/NH_4Cl-NH_3$ cycle.

◆ The output power of $CaCl_2$/ NH_4Cl-NH_3 cycle is not sensitive to the variation of output temperature (T_{sor} ≤ 55°C). Its effective discharging time even increases from about 65 to 90 min (40°C≤ T_{sor}≤55°C).

4. Results and discussion

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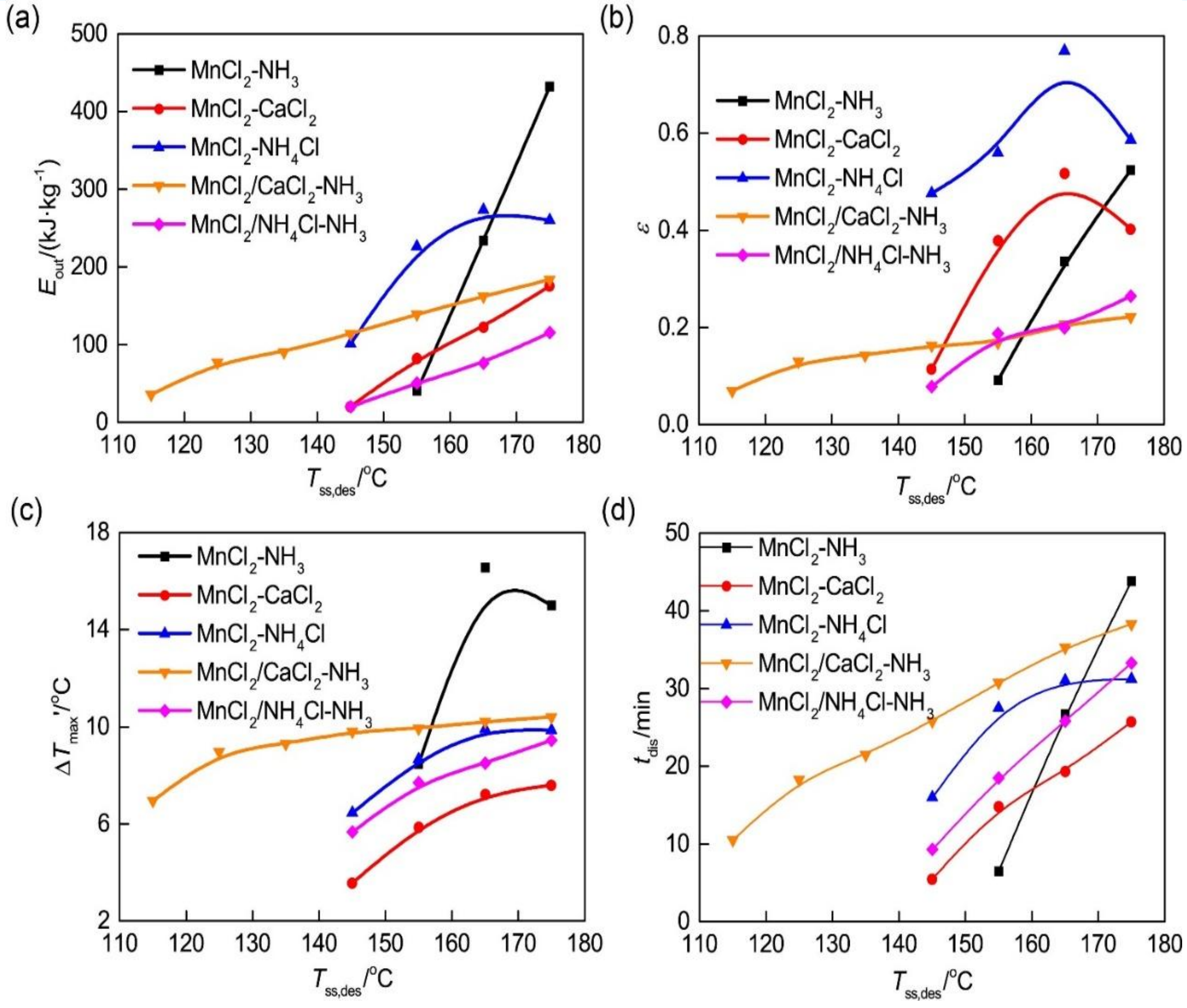
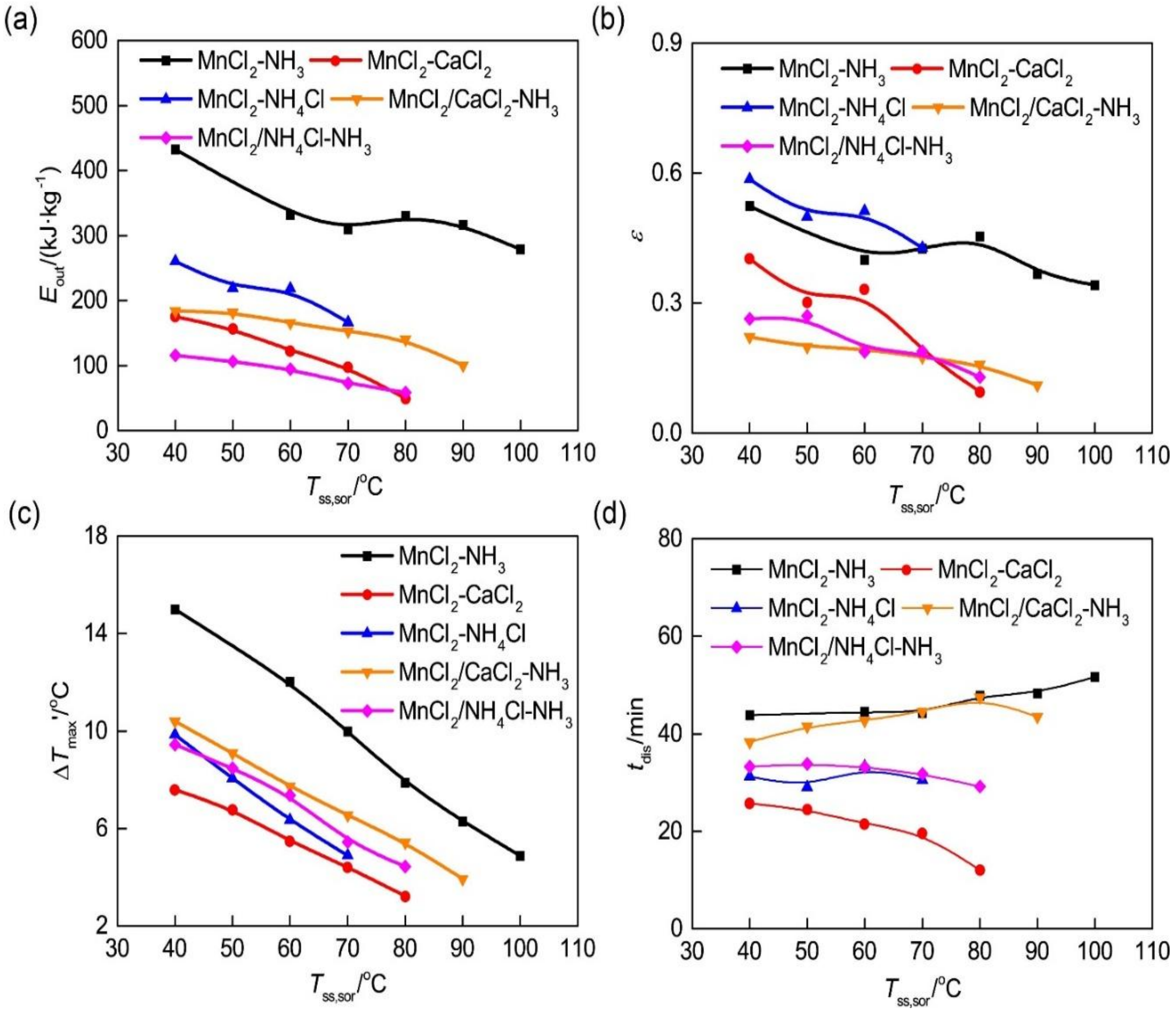
4.2 Cycle performance with **MnCl2/ENG-TSA** sorption bed as the output side

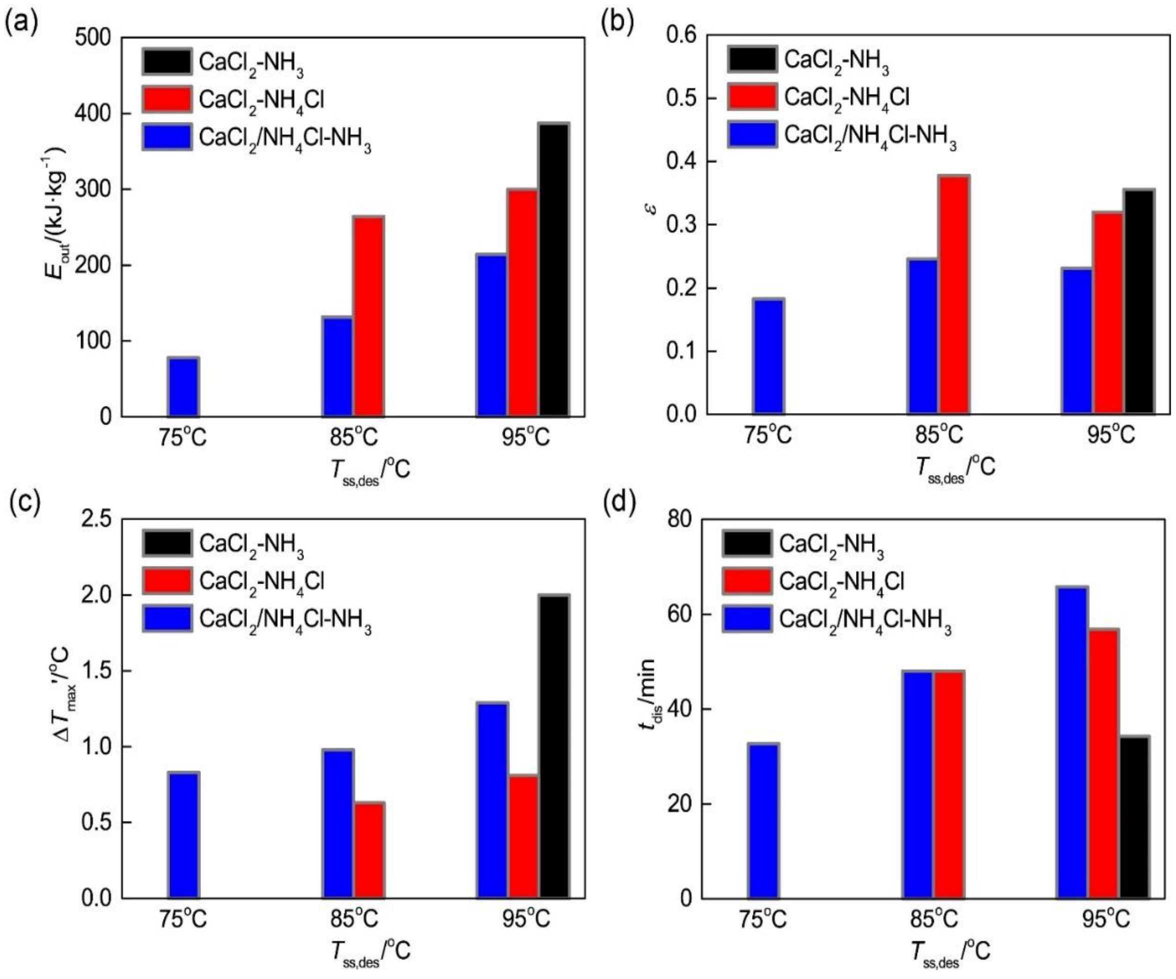


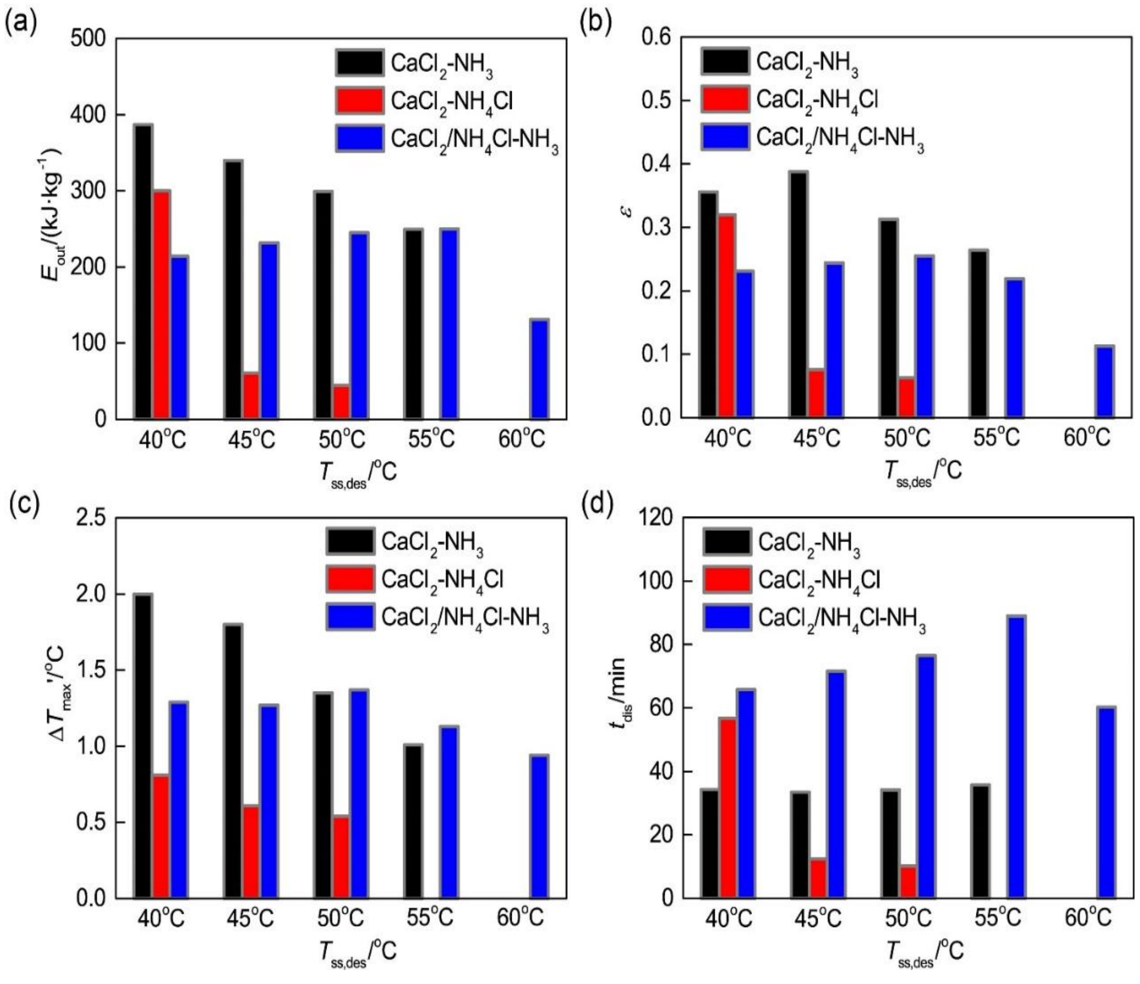


Heat source temperature($T_{ss,des}$) and output temperature ($T_{ss,sor}$) : (a) E_{out}, (b) ε , (c) ΔT_{max}', (d) t_{dis} .

4. Results and discussion

4.3 Cycle performance with **$CaCl_2$/ENG-TSA** sorption bed as the output side

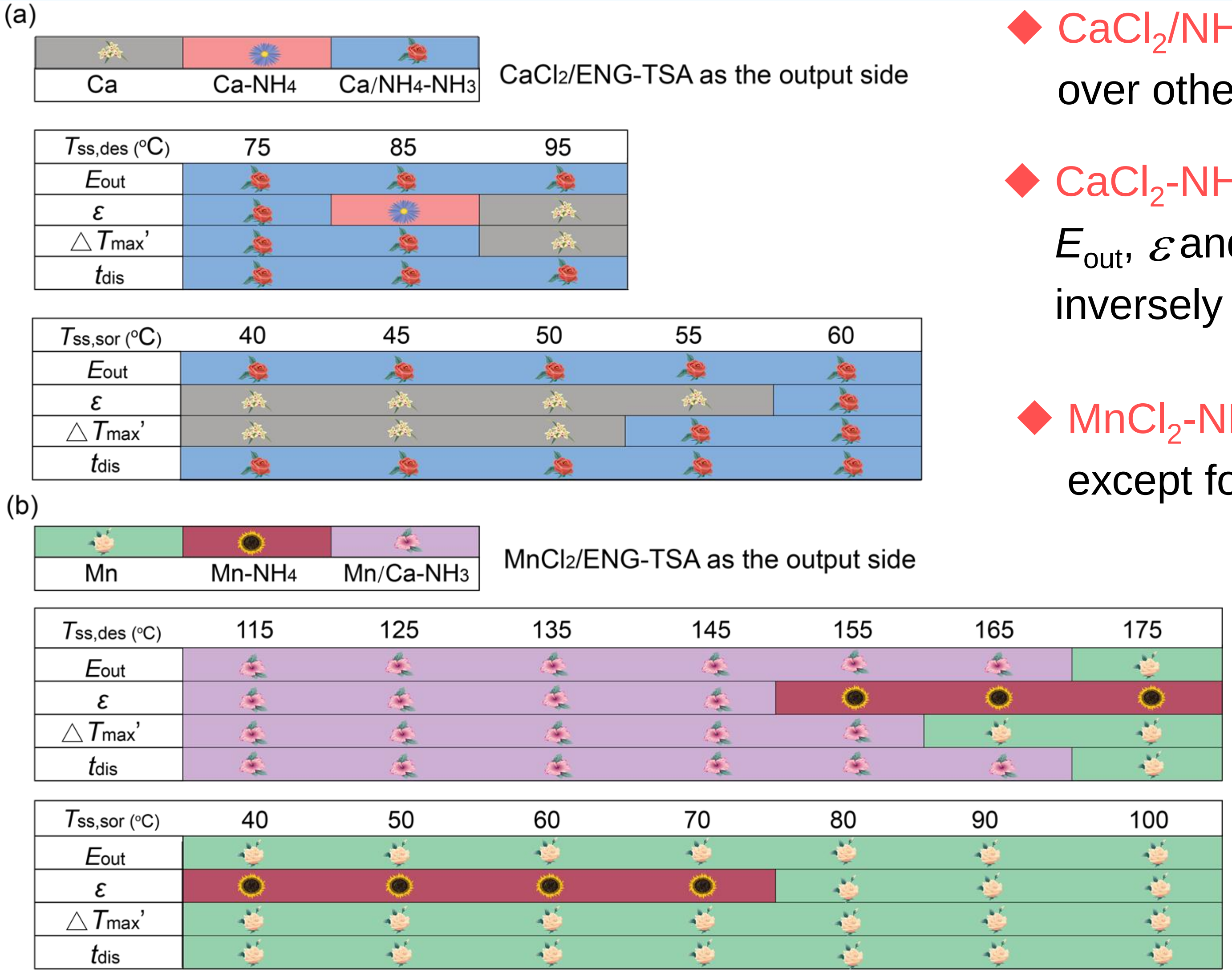




Heat source temperature($T_{ss,des}$) and output temperature ($T_{ss,sor}$) : (a) E_{out}, (b) ε , (c) ΔT_{max}', (d) t_{dis} .

4. Results and discussion

4.4 Overall evaluation of various cycles



(a)

Ca	Ca-NH4	Ca/NH4-NH3
⬜	🟥	🟦

CaCl2/ENG-TSA as the output side

$T_{ss,des}$ (°C)	75	85	95
E_{out}	🟦	🟦	🟦
ε	🟦	🟥	⬜
$\triangle T_{max}'$	🟦	🟦	⬜
t_{dis}	🟦	🟦	🟦

$T_{ss,sor}$ (°C)	40	45	50	55	60
E_{out}	🟦	🟦	🟦	🟦	🟦
ε	⬜	⬜	⬜	⬜	🟦
$\triangle T_{max}'$	⬜	⬜	⬜	🟦	🟦
t_{dis}	🟦	🟦	🟦	🟦	🟦

(b)

Mn	Mn-NH4	Mn/Ca-NH3
🟩	🟥	🟪

MnCl2/ENG-TSA as the output side

$T_{ss,des}$ (°C)	115	125	135	145	155	165	175
E_{out}	🟪	🟪	🟪	🟪	🟪	🟪	🟩
ε	🟪	🟪	🟪	🟪	🟥	🟥	🟥
$\triangle T_{max}'$	🟪	🟪	🟪	🟪	🟪	🟩	🟩
t_{dis}	🟪	🟪	🟪	🟪	🟪	🟪	🟩

$T_{ss,sor}$ (°C)	40	50	60	70	80	90	100
E_{out}	🟩	🟩	🟩	🟩	🟩	🟩	🟩
ε	🟥	🟥	🟥	🟥	🟩	🟩	🟩
$\triangle T_{max}'$	🟩	🟩	🟩	🟩	🟩	🟩	🟩
t_{dis}	🟩	🟩	🟩	🟩	🟩	🟩	🟩

Overall evaluation of various cycles based on E_{out}, ε , $\Delta T_{max}'$ and t_{dis}.

◆ $CaCl_2/NH_4Cl-NH_3$ cycle has absolute advantages on t_{dis} over other cycles.

◆ $CaCl_2-NH_3$ cycle will be the optimal choice considering E_{out}, ε and $\Delta T_{max}'$ ($T_{ss,des}$ =95°C and $T_{ss,sor}$≤ 50°C)), and inversely for $CaCl_2$/ NH_4Cl-NH_3 cycle.

◆ $MnCl_2-NH_3$ cycle is the optimal cycle ($T_{ss,des}$ =175°C), except for with $T_{ss,sor}$≤ 80°C.

◆ $MnCl_2-NH_4Cl$ cycle owns the largest ε (145≤$T_{ss,desm}$ ≤175 °C and 40≤$T_{ss,sor}$ ≤70°C).

◆ $MnCl_2/CaCl_2-NH_3$ cycle owns the largest E_{out}, $\Delta T_{max}'$ and longest t_{dis} ($T_{ss,des}$≤ 165°C).

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5. Conclusions

★ Resorption cycles and multi-stage cascading cycles can widen the working range for heat source temperature. $MnCl_2/CaCl_2-NH_3$ cycle exhibiting obvious merits over $MnCl_2/NH_4Cl-NH_3$ cycle.

★ For **low-temperature** heat source (≤ 90°C), $CaCl_2$/ENG-TSA sorption bed as the output side, the effective discharging time of $CaCl_2/NH_4Cl-NH_3$ cycle can reach up to 60 min. $CaCl_2-NH_3$ cycle will be the optimal choice with the maximum thermal storage density, efficiency and temperature lift of 400 $kJ \cdot kg^{-1}$, 0.39 and 2.0°C.

★ For **high-temperature** heat source ($115 \leq T_d \leq 175$°C), $MnCl_2$/ENG-TSA sorption bed as the output side, $MnCl_2-NH_3$ cycle is the optimal cycle ($165 \leq T_d \leq 175$°C), with the maximum thermal storage density, efficiency and temperature lift of 420 $kJ \cdot kg^{-1}$, 0.51 and 15.0°C. $MnCl_2/CaCl_2-NH_3$ cycle ($115 \leq T_d \leq 165$°C) owns the largest heat output density, temperature lift and effective discharging time of 140 $kJ \cdot kg^{-1}$, 10.0°C and 31 min.

Thanks！

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