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Performance Analysis of an Innovative Multimode, Multisalt and Multieffect Chemisorption Refrigeration System

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The conceptual design of an innovative multimode, multisalt and multieffect solid-gas chemisorption refrigeration system with evaporation and resorption processes is presented. In the proposed system, both the evaporation heat of the refrigerant during adsorption process and the reaction heat of the low-temperature salt during resorption process are employed to provide useful cooling. The reaction heat of the high-temperature salt is recovered for the regeneration process of the middle temperature salt. The presented system has the distinct advantage of larger cooling capacity per unit of heat input in comparison with other types of sorption refrigeration systems, based exclusively on evaporation or resorption. To identify the expected COP of the proposed system, two groups of working pairs containing metal chlorides and ammonia were analyzed. The ideal coefficient of performance (COP) can be improved by more than 59 to 169% if compared to the COP obtained with other kinds of cycle. When the sensible heats of the reactant, the refrigerant and the metallic part of the reactors are considered in the calculation of the COP, this figure can reach values between 0.91 and 1.80, according to the salts employed and the mass ratio between the metallic part of the reactor and the salt. © 2007 American Institute of Chemical Engineers *AIChE J,* 53: 3222–3230, 2007
Keywords: sorption refrigeration, heat recovery, adsorption, resorption

Introduction

Sorption refrigeration systems received considerable attention in recent years due to the increase of problems related to environmental pollution and energy scarcity.[1] These systems have lower environmental impact and large energy saving potential in comparison with conventional vapor compression refrigeration systems, because they neither use CFCs or HCFCs as working substances, nor use electricity as the main driving source.[2] Among the sorption refrigeration systems, liquid absorption units have been used extensively in the air conditioning market, while solid sorption systems are still mainly at the R&D stage. However, solid-gas sorption refrigeration has distinctive advantages over liquid-gas absorption refrigeration, due to its wider range of working temperature, higher storage capacity, and no problems with corrosion and crystallization.[3]

However, low coefficient of performance (COP), and specific cooling power (SCP) are the main drawbacks for the solid-gas sorption refrigeration systems. To overcome these problems, several means have been used, such as the better choice of adsorption working pairs, the improvement of the heat and mass transfer in reactive beds, the utilization of advanced cycles.[4] One of the approaches employed to solve the aforementioned problems is the utilization of compound adsorbents with porous materials and metal chloride salts. The former can be expanded graphite,[5–8] carbon fibers,[9,10]or activated carbon.[11,12] The high thermal conductivity of some porous materials, like expanded graphite, ensures good heat

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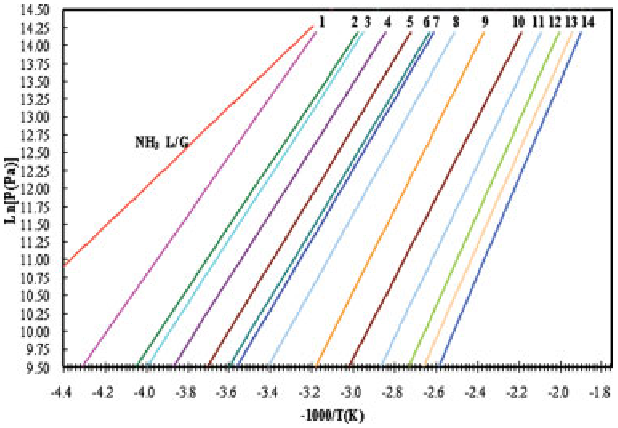

Figure 1. Equilibrium lines of chlorides reacting with ammonia.

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transfer, while the large porosity provides enough permeability for a suitable mass transfer.

Another possibility to enhance the heat transfer inside the reactor is the utilization of heat pipes.[13,14] Finally, many advanced cycles have been proposed and investigated to improve the performance of sorption refrigeration systems, e.g. cascading cycle,[15] thermal wave cycle,[16] forced convection cycle,[17] mass recovery cycle,[18] mass and heat recovery cycle,[19] and multistage cycle.[20] A special case of advanced cycle for chemisorption machines is based on the resorption process,[21–24] where the evaporator is replaced by a second solid-gas reactor, and the cooling occurs during desorption phase of the latter reactor. As the reaction heat is higher than the vaporization heat, the resorption process can achieve a higher cooling capacity than the conventional sorption process with a liquid-gas evaporator for a specified heat input, and, thus, achieve a higher COP.

In this article, an innovative multimode, multisalt and multieffect solid-gas chemical sorption refrigeration cycle, with internal heat recovery is proposed to improve the system COP. The reaction heat of the low-temperature salt (LTS) inside the reactor during the resorption phase, and the evaporation heat of the refrigerant inside evaporator during the adsorption phase provide useful cooling, and the reaction heat of the high-temperature salt (HTS) is recovered in the regeneration of the middle temperature salt (MTS). Moreover, the calculated COP of the proposed cycle was compared to the COP of a chemisorption cycle with only vaporization and with only resorption.

Solid-Gas Chemisorption Refrigeration System

Chemisorption refrigeration system with refrigerant evaporation

Solid-gas chemical sorption machines have their operation based on the thermal effects of reversible physicochemical processes between a salt and a refrigerant. Assuming ammonia as the refrigerant, the reactions can be described as

$$\begin{aligned} S\cdot nNH_3 + m\Delta H_R &\leftrightarrow S'\cdot(n-m)NH_3 + mNH_3(gas) \\ mNH_3(gas) &\leftrightarrow mNH_3(liq) + m\Delta H_{evap} \end{aligned} \tag{1}$$

There are a large amount of salts that react with ammonia. The Clapeyron diagram for some metal chlorides is shown in Figure 1, in which the solid-gas and liquid-gas equilibrium lines are given by the following equation

$$Ln(P_{eq}) = -\frac{\Delta H}{R_0 T_{eq}} + \frac{\Delta S}{R_0} \tag{2}$$

For chemical sorption refrigeration system, the synthesis and decomposition reactions take place when the salt is removed from the equilibrium condition of temperature and pressure.[25] The basic diagram of a solid-gas sorption system with liquid-gas evaporator is shown in Figure 2.

In order to reduce the heat input required to drive the system, Neveu and Castaing,[26] and Sorin et al.[27] proposed an internal heat recovery where the adsorption heat of one reactor was used in the regeneration of a second reactor, as shown in Figure 3.

Chemisorption refrigeration system with resorption process

In conventional sorption refrigeration systems, the useful cooling is obtained by the evaporation of refrigerant inside the evaporator, while in resorption systems, it is obtained from the desorption process in a second reactor. As the reaction enthalpy is

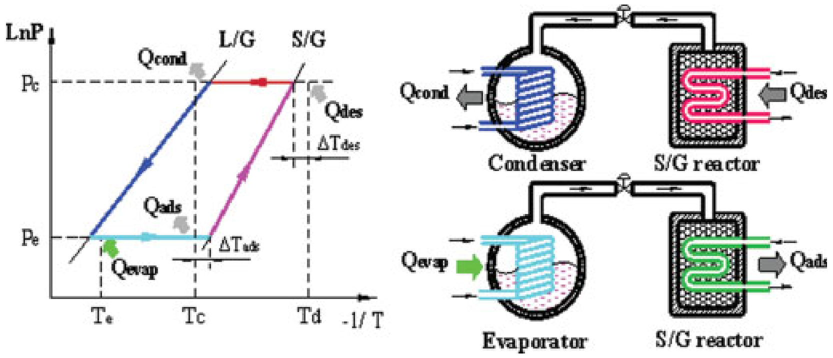

Figure 2. Chemisorption refrigerator.

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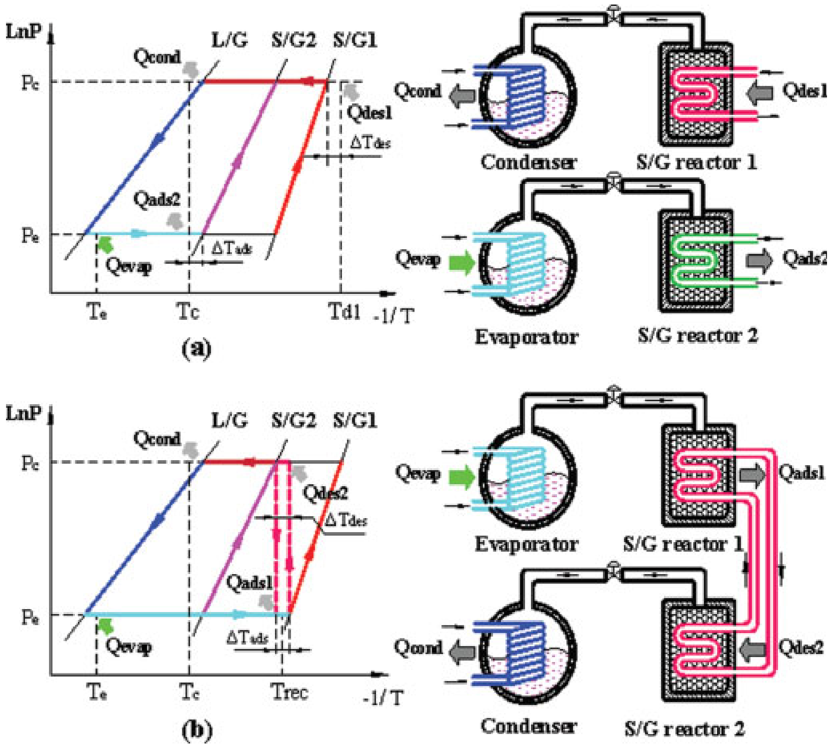

Figure 3. Internal heat recovery chemisorption refrigerator.

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about twice the value of the vaporization enthalpy, the resorption system can provide more cooling than a conventional sorption system, assuming that the same amount of refrigerant is being consumed or generated. Figure 4 shows the basic resorption cycle, which has been studied by many researchers.[21–24]

Resorption systems can also be benefited by internal heat recovery as proposed by Goetz et al.[21] To accomplish such a task, four reactors are filled with three different salts, and its working mode is shown in Figure 5. Reactor 1 is filled with high-temperature salt (HTS), and reactor 2 is filled with middle-temperature salt (MTS), while two other reactors contain the same low-temperature salt (LTS). When the HTS reactor is in adsorption mode and MTS reactor is in desorption operation, the reaction heat of former reactor is utilized in the generation process of the latter one.

An innovative multimode, multisalt and multieffect sorption refrigeration system

The conceptual design of a multisalt and multieffect sorption refrigeration system is proposed in this article to improve system performance. The Clapeyron diagram and schematic operation for the system without internal heat recovery is shown in Figure 6.

First, the HTS reactor is heated by an external heat source at high-temperature T_d and desorbs refrigerant to the con-

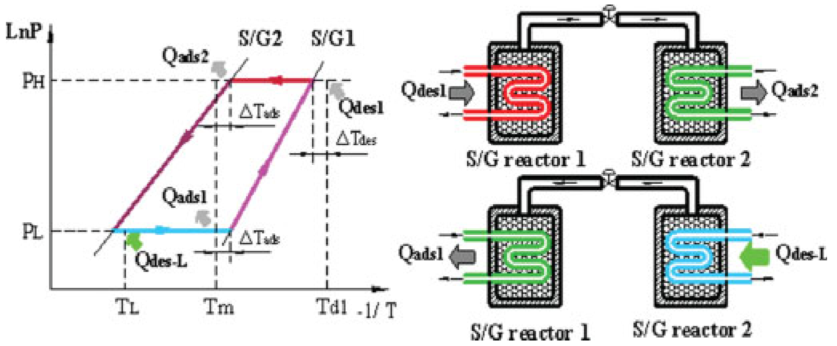

Figure 4. Chemisorption refrigerator with resorption process.

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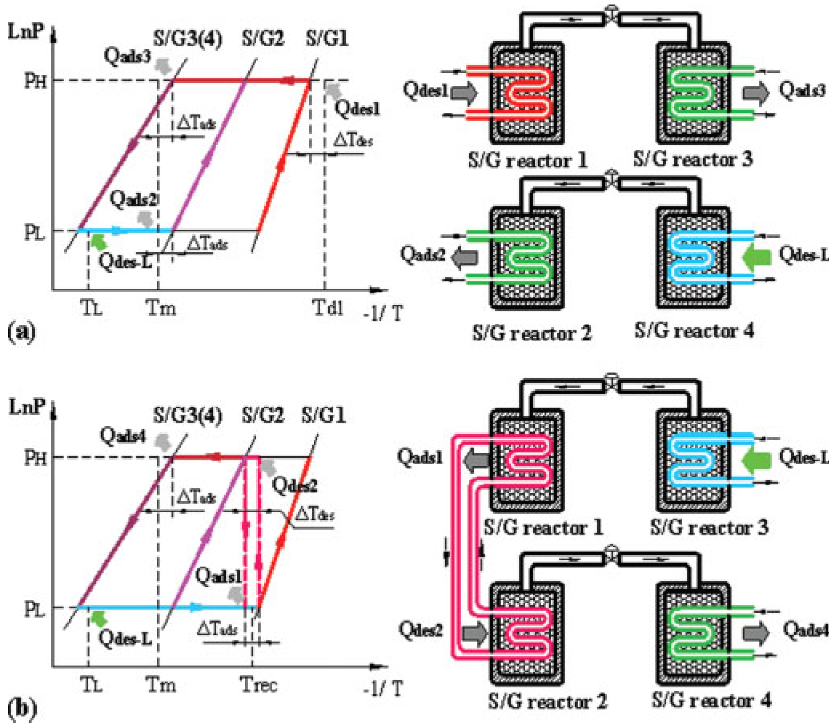

Figure 5. Internal heat recovery multisalt sorption refrigeration system with resorption process.

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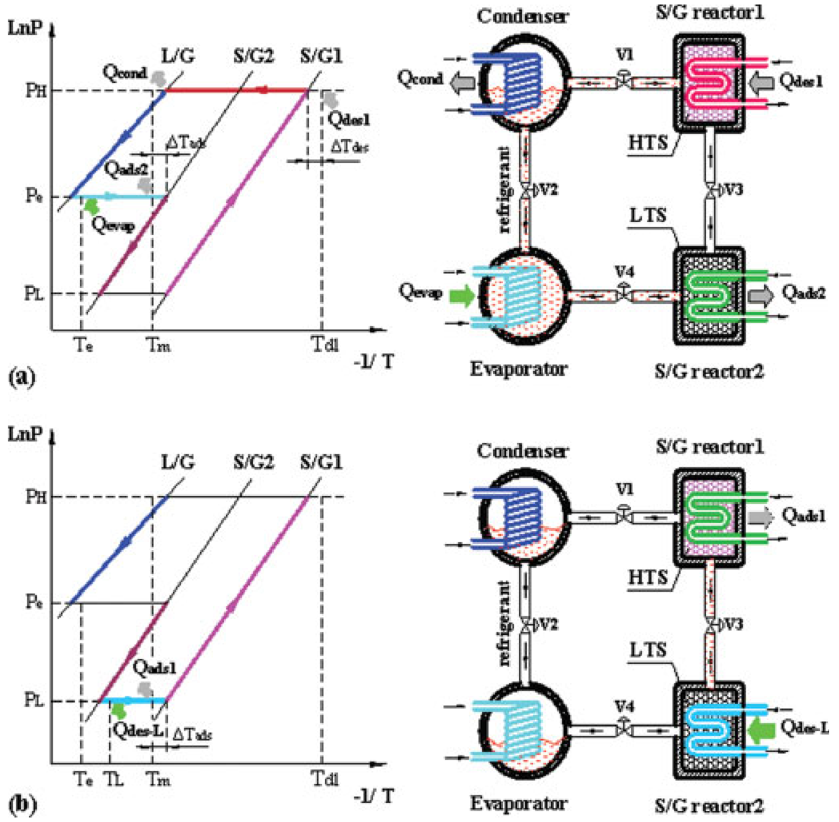

Figure 6. Double-effect sorption refrigeration system with evaporation and resorption processes.

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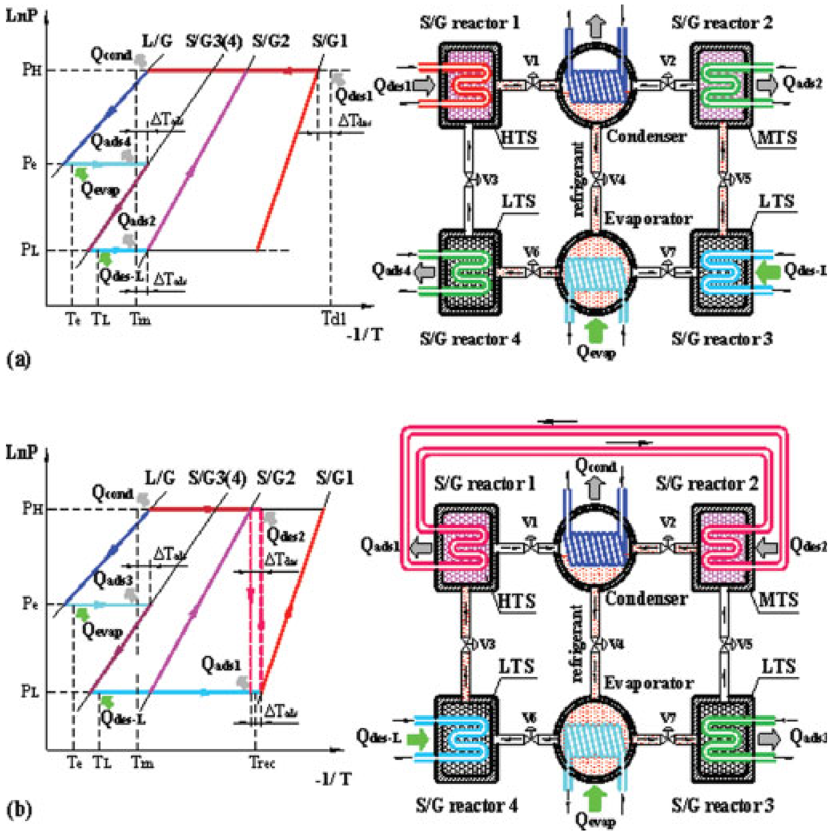

Figure 7. Internal heat recovery multisalt and multieffect sorption refrigeration system based on evaporation and resorption processes.

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denser, while the LTS reactor is cooled by a heat sink and adsorbs refrigerant from evaporator. The evaporation of refrigerant provides the cooling effect by extracting heat (Q_{evap}) from a chilled medium. Second, a resorption process takes place between the HTS and LTS, and the cooling effect occurs during the decomposition of the LTS.

When the heat recovery is considered for the improvement of the performance further, the system has four reactors, a condenser and an evaporator. One reactor is filled with high-temperature salt (HTS), and another is filled with middle-temperature salt (MTS), while other two reactors have low-temperature salts (LTS). The cycle operation has five thermodynamic processes, which include preheating, desorption, precooling, adsorption and resorption. The diagram of such a cycle, which can be divided in two phases, is shown in Figure 7 a and b.

In the first phase, the decomposition of the HTS inside the reactor 1 requires a heat input (Q_{des1}) from an external heat source at high-temperature T_{d1}, and the desorbed refrigerant condenses in the condenser by rejecting heat (Q_{cond}) at T_{m}. Simultaneously, the LTS reactor 4 is cooled by a heat sink to adsorb the refrigerant from the evaporator. The refrigerant vaporization produces a cooling effect at T_{e} by extracting heat (Q_{evap}) from a medium during the adsorption process. At the same time, a resorption process between the MTS reactor and LTS reactor 3 occurs, and a cooling effect is produced at low-temperature T_{L} by the absorption of heat ($Q_{\mathrm{des\text{-}L}}$) during the decomposition of the latter salt.

During the second phase, the working modes of the reactors are switched. The HTS reactor is in adsorption mode while the MTS reactor is under desorption. The LTS reactor 4 works as a pseudo-evaporator to provide a cooling effect during the resorption process between the HTS and the LTS. The refrigerant vapor flows from the LTS reactor 4 to the HTS reactor, and reacts with the salt, releasing the reaction heat (Q_{ads1}), and this energy is transferred for the regeneration of the MTS. During the heat recovery process, the MTS is heated from T_{a} to T_{d}, thus, the refrigerant pressure increases from synthesis level P_{L} to decomposition level P_{H}, and the refrigerant desorbed from the MTS reactor flows to the condenser. In this process, no external heat source is needed during the regeneration process of MTS. Simultaneously, the LTS reactor 3 adsorbs refrigerant from the evaporator, and produces another cooling effect. When compared to other kinds of sorption refrigeration systems, the presented system has the distinct advantage of larger cooling capacity per unit of heat input, due to the four cooling-effects obtained at the expense of only one heat input. Moreover, the proposed system can work as the sorption refrigeration system based on an evaporation process or on a resorption process.

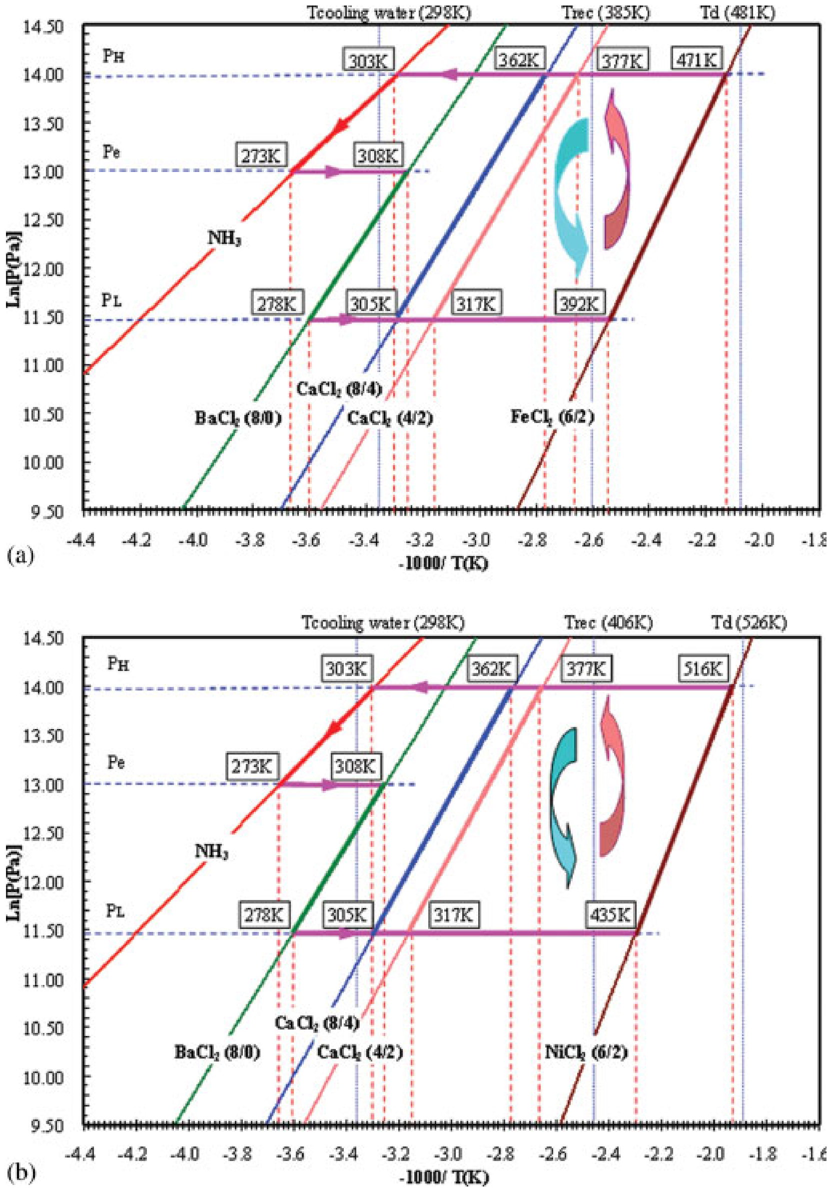

Figure 8. Clapeyron diagram of the multisalt and multieffect sorption refrigeration system with internal heat recovery.

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Performance analysis

The choice of the reactants is based on the salt equilibrium characteristics shown in Figure 1. For cooling production in the resorption refrigeration system, the reactor must generate refrigerant at low pressure and temperature. Figure 1 shows that there are only two salts ($PbCl_2$ and $BaCl_2$) that have decomposition temperatures below 273 K. However, the solid-gas equilibrium of $PbCl_2$ is closer to liquid-gas equilibrium of ammonia, which might lead to a high-risk of condensation in the tube between the two reactors or other parts of the system, during the adsorption phase of the LTS.

To assess the performance of the proposed system, two groups of working pairs were studied: (1) NH_3, $BaCl_2$, $CaCl_2$, $FeCl_2$, and (2) NH_3, $BaCl_2$, $CaCl_2$, $NiCl_2$, in which $FeCl_2$ and $NiCl_2$ are the high-temperature salts, $CaCl_2$ is the middle-temperature salt, and $BaCl_2$ is the low-temperature salt. The Clapeyron diagram for the two groups of working pairs, operating with the proposed cycle is shown in Figure 8.

The equilibrium equations for the LTS, MTS and for the two HTS, reacting with ammonia are shown in Eqs. 3 to 6, respectively

$$BaCl_2 + 8NH_3 \Leftrightarrow BaCl_2 \cdot 8NH_3 + \Delta H_{RL}$$
$$\Delta H_{RL} = 36.2kJ \cdot mol^{-1} \quad (3)$$

$$\begin{cases} CaCl_2 \cdot 2NH_3 + 2NH_3 \Leftrightarrow CaCl_2 \cdot 4NH_3 + \Delta H_{RM1} & \Delta H_{RM} = 40.9kJ \cdot mol^{-1} \\ CaCl_2 \cdot 4NH_3 + 4NH_3 \Leftrightarrow CaCl_2 \cdot 8NH_3 + \Delta H_{RM2} & \Delta H_{RM} = 39.6kJ \cdot mol^{-1} \end{cases} \quad (4)$$

$$FeCl_2 \cdot 2NH_3 + 4NH_3 \Leftrightarrow FeCl_2 \cdot 6NH_3 + \Delta H_{RH} \qquad \Delta H_{RH} = 50.2kJ \cdot mol^{-1} \quad (5)$$

$$NiCl_2 \cdot 2NH_3 + 4NH_3 \Leftrightarrow NiCl_2 \cdot 6NH_3 + \Delta H_{RH} \qquad \Delta H_{RH} = 56.7J \cdot mol^{-1} \quad (6)$$

The latent heat of vaporization of ammonia (ΔH_{evap}) at 273K is 21.4kJmol^{-1}.

Without considering the sensible heats of the salt, the refrigerant and the reactors, the ideal COP can be written as:

(1) For adsorption process with internal heat recovery

$$COP_i = 2 \cdot \Delta H_{evap} / \Delta H_R \quad (7)$$

(2) For resorption process with internal heat recovery

$$COP_i = 2 \cdot \Delta H_{RL} / \Delta H_{RH} \quad (8)$$

(3) For adsorption and resorption processes with internal heat recovery

$$COP_i = 2 \cdot \left(\Delta H_{RL} + \Delta H_{evap}\right) \Delta H_{RH} \quad (9)$$

The ideal COP of the three processes with internal heat recovery using the two groups of working pairs is shown in Figure 9. It can be seen that the multisalt and multieffect sorption refrigeration system, based on evaporation and resorption has the highest COP among the three kinds of systems. Compared to the system with only evaporation and to the system with only resorption, the proposed system can improve the ideal COP by more than 169 and 59%, respectively, when using $FeCl_2$ as the high-temperature salt. Moreover, the sorption system using $FeCl_2$ salt has higher COP than the system employing $NiCl_2$ salt, due to the lower reaction enthalpy of the former salt.

In order to obtain a more realistic estimation of the possible COP achieved by the proposed system, one should consider not only the reaction and vaporization heats, but also the sensible heat of the reactant, the refrigerant and the metallic part of the reactor. The COP obtained with the two working pair groups was calculated assuming an operation with the temperatures listed in Table1.

The useful cooling produced in the evaporator during the cycle was calculated by Eq. 10, and the cooling produced in the LTS reactor was calculated with Eq. 11

$$Q_{evap-cooling} = \left[n_1 \cdot \Delta H_{evap} - C^{liq}_{p-NH_3} M_{NH_3} (T_c - T_e) - C_{p-r} M_r (T_c - T_e) \right] \quad (10)$$

$$Q_{des-coolig} = \left[n_2 \cdot \Delta H_{RL} - C^{loaded}_{p-LTS} M_{LTS} (T_a - T_L) - C_{p-r} M_r (T_a - T_L) \right] \quad (11)$$

The heat input required for the decomposition of the MTS was calculated with Eq. 12, and for the decomposition of the HTS was calculated with Eq. 13

$$Q_{des2} = \left[n_3 \cdot \Delta H_{RM} + C^{loaded}_{p-MTS} M_{MTS} (T_{rec} - T_a) + C_{p-r} M_r (T_{rec} - T_a) \right] \quad (12)$$

$$Q_{des1} = \left[n_4 \cdot \Delta H_{RH} + C^{loaded}_{p-HTS} M_{HTS} (T_d - T_{rec}) + C_{p-r} M_r (T_d - T_{rec}) \right] \quad (13)$$

During synthesis phase, the heat released by the HTS reactor was calculated with the Eq. 14, and the expected COP was calculated with the Eq. 15

$$Q_{ads1} = \left[n_4 \cdot \Delta H_{RH} + C^{unloaded}_{p-HTS} M_{HTS} (T_d - T_{rec}) + C_{p-r} M_r (T_d - T_{rec}) \right] \quad (14)$$

$$COP_t = \frac{2 \times \left(Q_{evap-cooling} + Q_{des-cooling}\right)}{Q_{des1}} \quad (15)$$

Four groups of salts were analyzed, and the variation of COP with different mass ratio (R) between the metallic part of the reactor and the salt is presented in Figure 10.

It can be seen that the mass ratio R has a strong influence on the system performance. The COP decreases significantly as the mass ratio increases. In the range of mass ratio R from 0 to 15, the COP varies between 1.08 and 1.80 for the group of salt with NH_3, $BaCl_2$, $CaCl_2$ and $FeCl_2$.

In order to evaluate the internal heat recovery process, the necessary mass of each salt to desorb/adsorb/resorb 1kg of ammonia and the heat released/absorbed during these processes were calculated. The mass of salts are shown in Table 2. It was assumed that all the reactions would be 80% complete, because in real systems, to carry on the reaction to more than 80% of the maximum possible might increase considerably the cycle time.

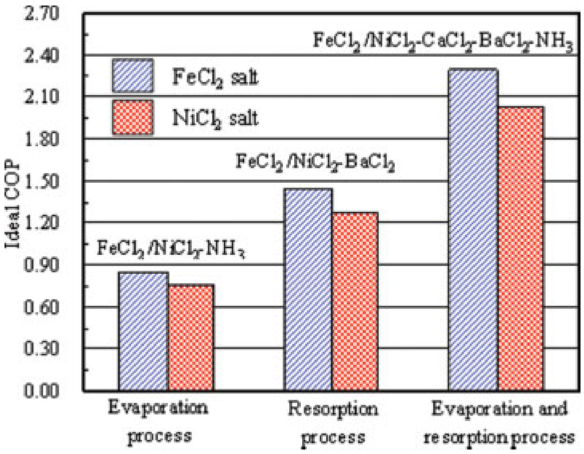

Figure 9. Ideal COP of three kinds of cycle with internal heat recovery.

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Table 1. Working Temperatures of the Adsorption and Resorption Cycle

Temperatures	Value
Evaporation temperature (T_e)	273 K
Condensation temperature (T_c)	303 K
Cooling water temperature ($T_{cooling}$)	298 K
Decomposition temperature of $BaCl_2$ (T_L)	278 K
Heat recovery temperature with $FeCl_2$ (T_{rec})	385 K
Heat recovery temperature with $NiCl_2$ (T_{rec})	406 K
Decomposition temperature of $FeCl_2$ (T_d)	481 K
Decomposition temperature of $NiCl_2$ (T_d)	516 K

The proposed heat recovery between the HTS and the MTS is only possible if the total amount of heat released by the HTS during the synthesis phase is equal or higher than the total heat input required during the regeneration phase of the MTS. The variation of the heat produced by the HTS and the heat consumed by the MTS with different mass ratio (R) between the metallic part of the reactor and the salt is shown in Figure 11.

It can be seen from Figure 11 that the heat production of HTS are higher than the heat consumption of MTS for the both groups of working pairs analyzed, which implies the reaction heat consumed by MTS can be supplied completely by the reaction heat released by the HTS. However, it is necessary to take some measures to keep the energy balance, and the extra heat released must be dissipated in another heat sink to ensure a proper operation of the system.

Conclusions

The conceptual design of an innovative multimode, multisalt and multieffect solid-gas chemisorption refrigeration system based on refrigerant evaporation and resorption process was presented. An internal heat recovery strategy was proposed to improve the system COP. In comparison with other types of sorption refrigeration systems based on only evaporation or resorption processes, this system has the distinct advantage of larger cooling capacity per unit of heat input.

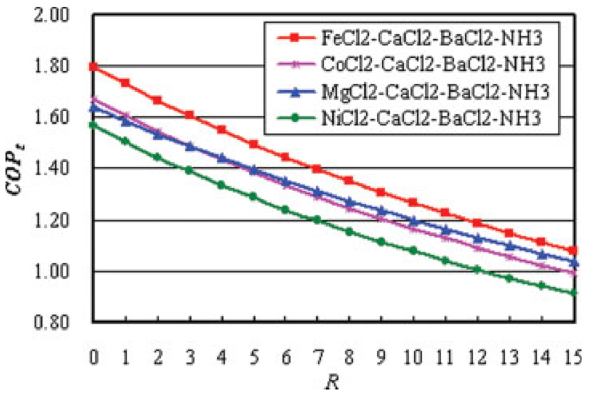

Figure 10. Variation of the COP with different mass ratio between the metallic part of the reactor and the salt.

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Table 2. Mass of Salt Necessary to Desorb/Absorb/Resorb 1 kg of Ammonia with 80% of the Reaction Completed

Parameters	Value
Mass of $BaCl_2$	1.91 $kg_{salt} \cdot kg_{NH_3}^{-1}$
Mass of $CaCl_2$	2.04 $kg_{salt} \cdot kg_{NH_3}^{-1}$
Mass of $FeCl_2$	2.33 $kg_{salt} \cdot kg_{NH_3}^{-1}$
Mass of $NiCl_2$	2.38 $kg_{salt} \cdot kg_{NH_3}^{-1}$

The ideal COP for the working pair group with $BaCl_2$, $CaCl_2$ and $FeCl_2$ is as high as 2.30, which is about 169 and 59% larger than the COP obtained in systems using only evaporation and resorption process, respectively. When the sensible heat of the reactant and other inert materials are considered in the calculation of the COP, the value ranged from 0.91 to 1.80, according to the salts employed and the mass ratio between the metallic part of the reactor and the salt.

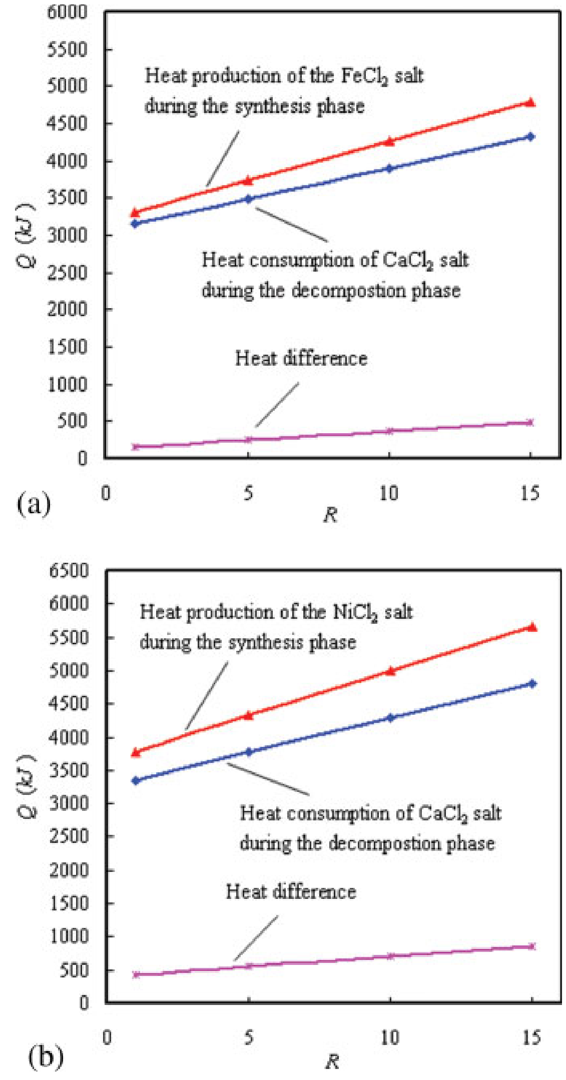

Figure 11. Heat production and heat consumption with different mass ratio between the metallic part of the reactor and the salt.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Acknowledgments

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Notation

COP = coefficient of performance
C_{p-HTS} = specific heat of HTS, $kJ/kg \cdot K$
C_{p-LTS} = specific heat of LTS, $kJ/kg \cdot K$
C_{p-MTS} = specific heat of MTS, $kJ/kg \cdot K$
C_{p-NH} = specific heat of ammonia, $kJ/kg \cdot K$
C_{p-r} = specific heat of reactant, $kJ/kg \cdot K$
HTS = high-temperature salt
LTS = low-temperature salt
MTS = middle temperature salt
M_{HTS} = mass of HTS reactor, kg
M_{LTS} = mass of LTS reactor, kg
M_{MTS} = mass of MTS reactor, kg
M_{NH_3} = mass of ammonia, kg
M_r = mass of reactant, kg
n_1 = number of moles of refrigerant cycled for evaporator
n_2 = number of moles of refrigerant cycled for LTS reactor
n_3 = number of moles of refrigerant cycled for MTS reactor
n_4 = number of moles of refrigerant cycled for HTS reactor
P_c = condensation pressure, Pa
Pe = evaporation pressure, Pa
P_{eq} = equilibrium pressure, Pa
P_H = high-pressure, Pa
P_L = low-pressure, Pa
Q_{ads} = adsorption heat, kJ
Q_{des} = desorption heat, kJ
$Q_{des\text{-}cooling}$ = desorption heat of LTS for cooling, kJ
$Q_{evap\text{-}cooling}$ = evaporation heat of refrigerant, kJ
R = mass ratio between the metallic mass of the reactor and the mass of salt
R_0 = universal gas constant, $kJ/mol \cdot K$
T_a = adsorption temperature, K
T_c = condensation temperature, K
$T_{cooling}$ = cooling water temperature, K
T_d = desorption temperature, K
T_e = evaporation temperature, K
T_{eq} = equilibrium temperature, K
T_L = desorption temperature of LTS, K
T_{rec} = recovery temperature, K

Greek letters

ΔH = enthalpy of transformation, kJ/mol
ΔH_{evap} = vaporization enthalpy of refrigerant, kJ/mol
ΔH_R = reaction enthalpy of reactant, kJ/mol
ΔH_{RL} = reaction enthalpy of LTS, kJ/mol
ΔH_{RM} = reaction enthalpy of MTS, kJ/mol
ΔH_{RH} = reaction enthalpy of HTS, kJ/mol
ΔS = entropy of transformation, $kJ/mol \cdot K$
ΔT_{eq} = equilibrium temperature drop, K

Subscripts

i = ideal
t = theoretical

Superscripts

liq = liquid state
$loaded$ = loaded state
$unloaded$ = unloaded state

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