A Target-Oriented Solid-Gas Thermochemical Sorption Heat Transformer for Integrated Energy Storage and Energy Upgrade

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An innovative target-oriented solid-gas thermochemical sorption heat transformer is developed for the integrated energy storage and energy upgrade of low-grade thermal energy. The operating principle of the proposed energy storage system is based on the reversible solid-gas chemical reaction whereby thermal energy is stored in form of chemical bonds with thermochemical sorption process. A novel thermochemical sorption cycle is proposed to upgrade the stored thermal energy by using a pressure-reducing desorption method during energy storage process and a temperature-lift adsorption technique during energy release process. Theoretical analysis showed that the proposed target-oriented thermochemical sorption heat transformer is effective for the integrated energy storage and energy upgrade, and the low-grade thermal energy can be upgraded from 87 to 171°C using a group of sorption working pair $MnCl_2$-$CaCl_2$-NH_3. *Moreover, it can give the flexibility of deciding the temperature magnitude of energy upgrade by choosing appropriate sorption working pairs.* © 2012 American Institute of Chemical Engineers *AIChE J,* 59: 1334–1347, 2013

Keywords: thermochemical sorption, heat transformer, energy storage, energy upgrade, low-grade thermal energy

Introduction

Energy shortage is currently becoming an urgent problem as the increasing industrialization and modernization of the world with a growing energy demand.[1] It seems that advanced energy-saving technology is one of potential methods to alleviate the intractable issue. Usually, the energy consumption of various industrial plants accounts for more than 60% of the total national energy consumption. Thus, it is very important to improve energy utilization efficiency for the sustainable development with economic benefits. At the same time, there exists an enormous amount of low-grade energy resources from industrial processes in many plants, such as petroleum and chemical plant, iron and steel plant, nuclear power plant, and coal-fired power plant. These low-grade energy resources include industrial waste heat, low-temperature condensation water, chimney exhaust of furnace, and exhaust gases from engines, and so on.[2]

However, a large amount of low-grade waste heat is usually released directly to the atmosphere or surface water without rational reutilization in many industrial plants due to the lack of efficient recovery methods and their low temperatures, which cannot meet the high temperature requirement in most industrial processes.[3] These discarded waste heat would become the negative thermal pollution for the environment. Whereas, the low-grade waste heat would become useful energy resources if they can be reutilized, and can contribute to reduce primary energy consumption and promote industrial development at low capital cost. Thus, it is desirable to attempt to recycle the low-grade waste heat as efficiently as possible and upgrade them to higher-temperature by developing advanced heat transformer technologies. Heat transformer plays a crucial role in the industrial heat recovery of low-grade energy resources to improve energy efficiency, and it is effective for upgrading the temperature of low-grade heat to a higher useful temperature level. For successful recovery and utilization of low-grade energy resources, both energy storage and energy upgrade technologies are necessary.[4]

The common ways used for energy upgrade using thermal-powered heat transformer is the liquid-gas absorption heat transformer, solid-gas physical adsorption heat transformer, and solid-gas thermochemical sorption heat transformer (or solid-gas reaction heat transformer).[5–7] In comparison with absorption and physical adsorption heat transformer, thermochemical sorption heat transformer has the advantages of no crystallization and solution corrosion problems, simple component, larger amount of reaction heat for high-energy density, stable working temperature, adaptability to the wide range of working temperature, and so on.[8] Therefore, solid-gas thermochemical sorption heat transformer has the attractive potential of better commercial value and extensive application among these heat transformers, and it is more suitable for the energy upgrade of different low-grade heat sources in the industrial heat recovery systems, because it has wide candidates of sorption working pairs and the monovariant characteristic of chemical reaction for keeping stable operating temperature,[9] in which different sorption working pairs have different heat input temperatures during energy consumption phase. Thus, it can use thermal energy efficiently by selecting appropriate sorption working pairs according to the external heat sources at different working temperatures.

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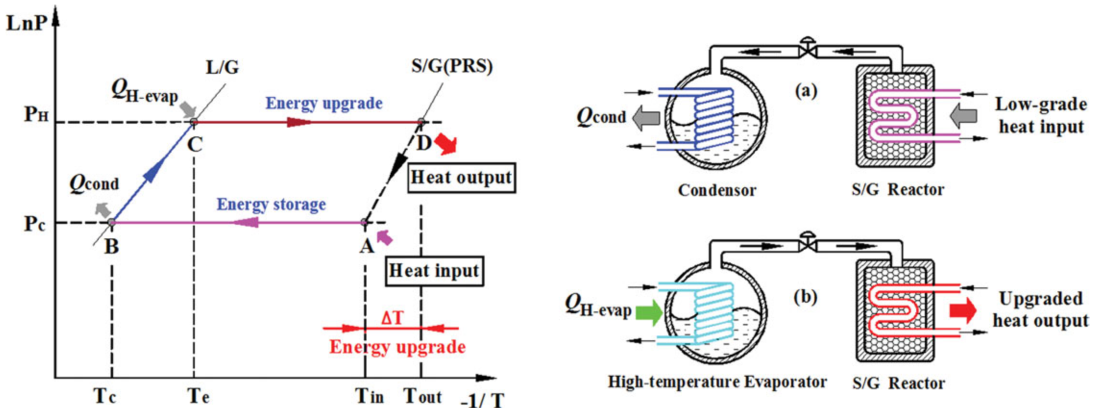

Figure 1. Schematic diagram of solid-gas thermochemical sorption heat transformer based on temperature-lift adsorption process.

(a) Energy storage process of low-grade thermal energy; (b) energy release process for energy upgrade using temperature-lift adsorption technique. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In solid-gas thermochemical sorption heat transformer, thermal energy is stored and upgraded using decomposition and synthesis reaction processes between a sorption material and a gas.[10] Usually, basic thermochemical sorption heat transformer has low-temperature upgrade capacity, and the heat released is mostly used to supply hot water for residential heating. Thus, the low-energy upgrade capacity is the main drawback for these energy systems, which has been still hindering its extensive industrial application for the reutilization of low-grade waste heat. To improve energy upgrade capacity, a thermochemical resorption heat transformer was proposed using two different salts,[11] in which the condenser/evaporator is replaced by a second solid-gas reactor. Thermochemical resorption heat transformer has higher-energy upgrade capacity and working reliability when compared with thermochemical adsorption heat transformer, and it has an appropriate operating pressure and thus can avoid the safety problem caused by the high pressure.[12] However, thermochemical adsorption heat transformer has the advantage of stable heat output temperature during energy release process in comparison with thermochemical resorption heat transformer. To further improve the energy upgrade capacity, some advanced thermochemical adsorption or resorption heat transformers were developed using two/multireactors filled with different salts,[13,14] in which internal heat recovery processes are performed between different reactors. Research showed the working performances can be improved at different extents, but these systems are complicated and have low reliability.

However, there exist some inherent shortcomings for aforementioned thermochemical adsorption or resorption heat transformer during the operating process. For thermochemical adsorption heat transformer system, temperature upgrade is achieved by lifting the operating pressure of working gas, and the temperature magnitude of energy upgrade is nearly proportional to the pressure-lift extent of the gas. The high-operating pressure is the common drawback and it may cause the safety problem when a high-heat output temperature is required during energy release process.[8] Thus, to keep a reasonable working pressure, the energy upgrade capacity of thermochemical adsorption heat transformer is usually low. Moreover, the heat input temperature is relatively high during energy storage process. Therefore, these energy systems cannot operate when the available low-grade heat source temperature is rather low.[15] For thermochemical resorption heat transformer systems, the heat input temperature can be decreased during energy storage process and the energy upgrade capacity can be improved efficiently. However, the heat output temperature usually fluctuates and decreases during energy release process due to the oscillation of system operating pressure, which is caused by the mismatch of chemical reaction rates in different reactors.[8,16] Thus, it is very difficult to realize the close match between the energy supply and the energy demand because of the unstable heat output temperature.

In this article, an innovative target-oriented solid-gas thermochemical sorption heat transformer is proposed which can overcome the drawbacks by combining the merits of thermochemical adsorption and resorption heat transformers. Low-grade thermal energy is stored in form of chemical bonds resulting from solid-gas sorption processes, and the integrated energy storage and energy upgrade can be accomplished using the same sorption system. A pressure-reducing desorption method is used to improve energy upgrade capacity by lowering heat input temperature during energy storage process, and a temperature-lift adsorption technique is used to further enhance energy upgrade capacity and to avoid the fluctuation of heat output temperature during energy release process. The working performance and thermodynamic characteristics of the proposed target-oriented thermochemical sorption heat transformer for integrated energy storage and energy upgrade are analyzed and discussed.

Description of the Innovative Solid-Gas Thermochemical Sorption Heat Transformer for Integrated Energy Storage and Energy Upgrade

Solid-gas thermochemical sorption heat transformer based on temperature-lift adsorption process (TSHT-1Salt-L/G)

The working principle of solid-gas thermochemical sorption heat transformer based on temperature-lift adsorption process is illustrated in Figure 1. It is mainly comprises of a solid-gas (S/G) reactor and a refrigerant vessel. The refrigerant vessel works as a condenser during energy storage phase and works as a high-temperature evaporator during energy release phase. The operating process of this kind of heat transformer is as follows

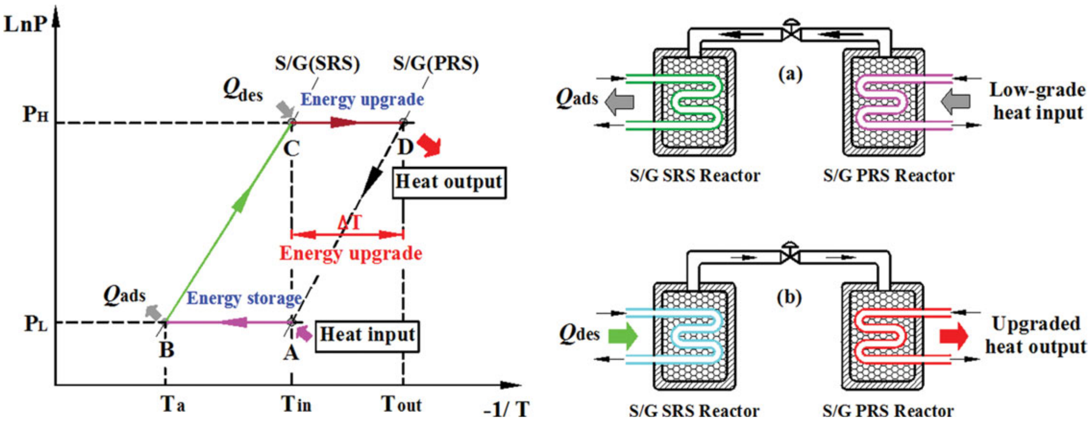

Figure 2. Schematic diagram of solid-gas thermochemical sorption heat transformer based on pressure-reducing desorption process.

(a) Energy storage process of low-grade thermal energy using pressure-reducing desorption technique; (b) energy release process of stored low-grade thermal energy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

During energy storage phase (A-B), the S/G reactor is heated by an external low-grade heat source at a temperature T_{in} and the refrigerant is desorbed to the condenser. The low-grade thermal energy is stored in form of chemical bonds arising from the desorption process, and the desorbed liquid refrigerant is stored in the refrigerant vessel.

During energy upgrade phase (B-C-D), a temperature-lift adsorption method is used to upgrade the stored thermal energy. The liquid refrigerant is first heated to raise its working temperature from the condensation temperature to a higher-evaporation temperature (B-C), and then the refrigerant evaporates and flows to the S/G reactor to react with salt (C-D). The chemical reaction heat released during synthesis reaction process supplies thermal energy for end user application at a temperature T_{out}. Due to the temperature-lift adsorption process, the evaporation pressure P_H during energy release phase is higher than the condensation pressure P_c during energy storage phase, thus, the heat output temperature becomes higher than the heat input temperature due to the monovariant characteristic of solid-gas chemical reaction. The low-grade thermal energy can be upgraded from T_{in} to T_{out}, and the temperature magnitude of energy upgrade is expressed as: $\Delta T = T_{out} - T_{in}$.

For solid-gas thermochemical sorption heat transformer based on temperature-lift adsorption process, it has the advantage that the heat output temperature is stable during energy release phase because the operating pressure is controlled by the evaporation pressure of the refrigerant. Therefore, it is easy to keep a good match of energy supply and energy demand for end user. However, thermochemical sorption heat transformer based on temperature-lift adsorption process has the disadvantage of low-temperature upgrade of low-grade thermal energy because the evaporation pressure is unsuitable to keep too high in consideration of the safe operation.

Solid-gas thermochemical sorption heat transformer based on pressure-reducing desorption process (TSHT-2Salts)

The working principle of solid-gas thermochemical sorption heat transformer based on pressure-reducing desorption process is shown Figure 2. It consists of two reactors: a S/G primary reactor with a primary reactive salt (PRS) and a S/G secondary reactor with a secondary reactive salt (SRS). At the same working pressure, the PRS has a higher-equilibrium temperature than SRS. The operating process of this kind of heat transformer is as follows

During energy storage phase (A-B), a pressure-reducing desorption method is used to store the thermal energy. The secondary reactor is used to lower the heat input temperature of the primary reactor during the regeneration phase of PRS, in which the primary reactor performs decomposition chemical reaction while the secondary reactor undergoes synthesis chemical reaction. The PRS is heated by external heat source at a temperature T_{in} to desorb the refrigerant to the SRS, and the low-grade thermal energy is stored in form of chemical bonds resulting from the desorption process between the PRS and the SRS. Especially, the heat input temperature during energy storage phase can be lowered effectively due to the pressure-reducing desorption process. Thus, it can widen the working temperature range of thermal energy from the external low-grade heat source.

During energy upgrade phase (B-C-D), the secondary reactor is heated by external heat source at a temperature T_{in} to desorb the refrigerant to the primary reactor. The SRS performs decomposition chemical reaction while the PRS undergoes synthesis chemical reaction, in which the refrigerant flows from the secondary reactor to the primary reactor and reacts with the PRS. During synthesis, chemical reaction heat released is used to supply the thermal energy for end user at a temperature T_{out}. Due to the pressure-reducing desorption process, the working pressure during energy release phase P_H is higher than the working pressure P_L during energy storage phase, thus, the heat output temperature becomes higher than the heat input temperature due to the monovariant characteristic of solid-gas chemical reaction. The low-grade thermal energy can be upgraded from T_{in} to T_{out},and the temperature magnitude of energy upgrade is expressed as: $\Delta T = T_{out} - T_{in}$.

For solid-gas thermochemical sorption heat transformer based on pressure-reducing desorption process, it has the advantage that the heat input temperature can be lowered effectively during energy storage phase due to the pressure-reducing technique. Thus, it can widen the working temperature range of low-grade heat source. In comparison with the aforementioned temperature-lift adsorption technique, the pressure-reducing technique has an appropriate working pressure and the magnitude of temperature upgrade is usually

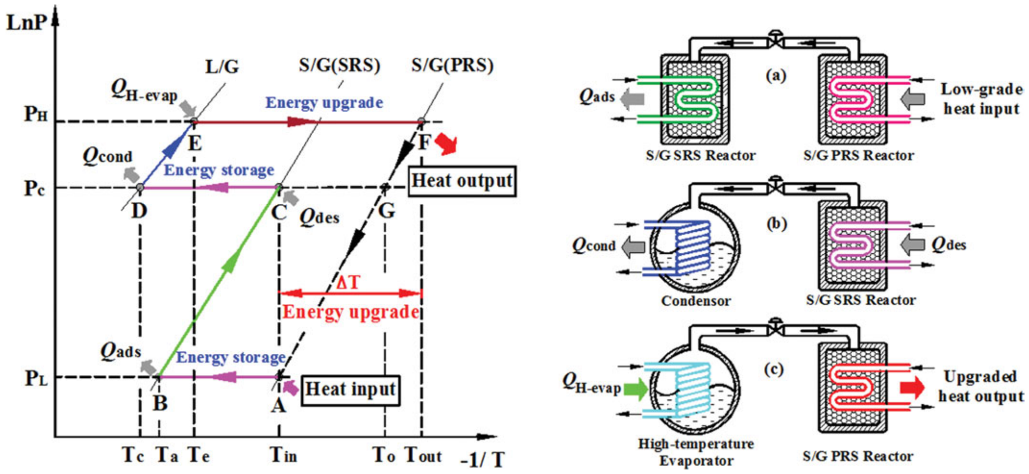

Figure 3. Schematic diagram of solid-gas thermochemical sorption heat transformer based on pressure-reducing desorption and temperature-lift adsorption processes.

(a) Energy storage process of PRS reactor using pressure-reducing desorption technique; (b) energy storage process of SRS reactor; (c) Energy release process for energy upgrade using temperature-lift adsorption technique. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

high. However, it has disadvantage that the heat output temperature fluctuates due to the oscillation of working pressure caused by the mismatch of the decomposition reaction rate of SRS and the synthesis reaction rate of PRS. Thus, it is difficult to keep good match between energy supply and energy demand for end user.

Solid-gas thermochemical sorption heat transformer based on pressure-reducing desorption and temperature-lift adsorption processes (TSHT-2Salts-L/G)

To overcome the shortcomings existed in the aforementioned heat transformer, an innovative solid-gas thermochemical sorption heat transformer based on pressure-reducing desorption and temperature-lift adsorption processes is developed. The working principle of the proposed new solid-gas thermochemical sorption heat transformer is shown Figure 3. A pressure-reducing desorption technique is used to lower the heat input temperature during energy storage phase and a temperature-lift adsorption technique is used to avoid the fluctuation of the heat output temperature during energy release process.

The system mainly consists of an S/G primary reactor operating at a high temperature, an S/G secondary reactor operating at a middle temperature, and a refrigerant vessel. The refrigerant vessel works as a condenser during energy storage phase and works as a high-temperature evaporator during energy release phase. To accomplish the integrated energy storage and energy upgrade of low-grade thermal energy, two different reactive salts are used in the two solid-gas reactors. The primary reactor is filled with a PRS with a higher-equilibrium temperature than the SRS filled inside the secondary reactor at the same operating pressure. Thus, the two reactive salts are referred to as the PRS and the SRS, respectively.

During energy storage phase (A-B-C-D), a pressure-reducing desorption method is used to lower the heat input temperature form the external heat source, and the low-grade thermal energy is stored in form of chemical bonds with the sorption process. The energy storage process consists of two operating stages. The first stage is the regeneration phase of the PRS (A-B), in which the S/G secondary reactor is used to lower the heat input temperature of the S/G primary reactor. The PRS is heated by low-grade thermal energy at a temperature T_{in} to desorb the refrigerant to the SRS. The second stage is the regeneration phase of the SRS (B-C-D), in which the SRS is heated to desorb the refrigerant to the condenser. The heat input temperature can be effectively decreased from T_o to T_{in} during the energy storage phase due to the pressure-reducing desorption method. Thus, it can widen the working temperature range of thermal energy from low-grade heat source.

During energy upgrade phase (D-E-F), a temperature-lift adsorption method is proposed to upgrade the stored thermal energy. The liquid refrigerant is first heated by a second heat source to lift its temperature form the condensation temperature to a higher-evaporation temperature (D-E), and then it evaporates at a high pressure P_H and flows to the primary reactor to react with the PRS (E-F). The chemical reaction heat released during the synthesis reaction process of PRS is used to supply the thermal energy for end user at a temperature T_{out}.

It is noteworthy to mention that the second heat consumption during the temperature–lift adsorption process can be supplied by the external low-grade heat source or additional heat source with lower-temperature (such as solar energy and condensation water). Moreover, the synthesis reaction heat released by the secondary reactor-condenser (in fact it works as a low-temperature evaporator) can also be recovered and used as the second heat source for the high-temperature evaporator-primary reactor during energy release phase to produce higher-thermal energy for end user. The working principle can be referred from the internal heat recovery process.[17,18]

Moreover, it can be seen that the working pressure P_H during energy release phase is much higher than the working pressure P_L during energy storage phase because both pressure-reducing desorption process and temperature-lift adsorption process are performed together. Thus, the heat output temperature becomes large higher than the heat input temperature. This is because the low-grade thermal energy can be first upgraded from T_{in} to T_o by using the pressure-reducing desorption process, and then it can be further upgraded from T_o to T_{out} by using temperature-lift adsorption process. The total temperature magnitude of energy upgrade is expressed as: $\Delta T = T_{out}\text{-}T_{in}$.

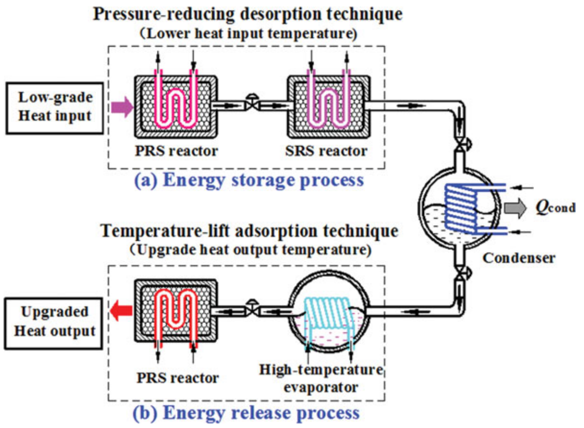

Figure 4. Schematic diagram of the physical arrangement of system components of the innovative solid-gas thermochemical sorption heat transformer for integrated energy storage and energy upgrade of low-grade thermal energy.

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

Figure 4 shows the physical arrangement of system components of the innovative solid-gas thermochemical sorption heat transformer for the integrated energy storage and energy upgrade of low-grade thermal energy. The proposed thermochemical sorption transformer has distinct advantages of higher-energy upgrade capacity and stable heat output temperature when compared with the thermochemical sorption heat transformer based on temperature-lift adsorption process or pressure-reducing desorption process. As shown in Figure 3, in comparison with thermochemical sorption heat transformer based on temperature-lift adsorption process (G-D-E-F), the working pressure can be decreased from the saturation condensation pressure of the refrigerant (P_c) to the equilibrium pressure of the SRS (P_L) during energy storage process when the pressure-reducing desorption regeneration method is introduced in the proposed thermochemical sorption energy storage system (A-B-C-D-E-F), and the heat input temperature can be decreased from T_o (point G) to T_{in} (point A), thus, it is beneficial to widening the temperature range of low-grade thermal energy. In addition, for the thermochemical sorption heat transformer based on temperature-lift adsorption process, the working pressure would become very high during energy release phase when higher-heat output temperatures is required for end user. This is because the increasing rate of the equilibrium temperature of ammonia is higher than that of the equilibrium temperature of reactive salt as shown in Figure 5. Especially, the problem would become more serious when the evaporation temperature is higher than 50°C, thus, the temperature magnitude of energy upgrade is limited in the thermochemical sorption heat transformer based on temperature-lift adsorption process.

In comparison with thermochemical sorption heat transformer based on pressure-reducing desorption process (A-B-C-G), the working pressure can be increased from the equilibrium pressure of SRS (P_c) to the high-evaporation pressure of refrigerant (P_H) during energy release process when the temperature-lift adsorption method is introduced in the proposed thermochemical sorption energy storage system (A-B-C-D-E-F), and the heat output temperature can be upgraded from T_o (point G) to T_{out} (point F), thus, it is beneficial to further enhancing the energy upgrade capacity. In addition, the proposed thermochemical sorption transformer can improve the working reliability by changing the energy supply mode during energy release phase, in which the operating pressure is controlled by the evaporator to keep a stable working pressure. Therefore, the proposed system can overcome the drawback such as the fluctuation of operating pressure and the decrease of heat output temperature caused by the mismatch of chemical reaction rates of different salts existed in the thermochemical sorption heat transformer based on pressure-reducing desorption process.

Thermodynamic Analysis of the Innovative Solid-Gas Thermochemical Sorption Heat Transformer

To achieve the integrated energy storage and energy upgrade of low-grade thermal energy, the sorption working pairs suitable for the innovative thermochemical sorption heat transformer are selected based on the thermodynamic equilibrium characteristics of different reactive salts, in which metal chloride/metal bromide-ammonia are preferred as the potential working pairs. A group of working pair of NH_3, NaBr, and $MnCl_2$ is chosen as an example to show the advantages and operating principle of the proposed innovative thermochemical sorption heat transformer. $MnCl_2$ is used as the PRS, NaBr is used as the SRS, whereas NH_3 is the refrigerant.

For the PRS, the reaction equation between manganese chloride and ammonia is

$$MnCl_2 \cdot 2NH_3 + 4NH_3 \leftrightarrow MnCl_2 \cdot 6NH_3 + \Delta H_{PRS} \quad (1)$$

For the SRS, the reaction equation between sodium bromide and ammonia is

$$NaBr + 5.25NH_3 \leftrightarrow NaBr \cdot 5.25NH_3 + \Delta H_{SRS} \quad (2)$$

in which the reaction enthalpy ΔH_{PRS} and entropy ΔS_{PRS} of $MnCl_2$ are 47,416 J mol^{-1} and 227.9 J mol^{-1} K^{-1}; the reaction enthalpy ΔH_{SRS} and entropy ΔS_{SRS} of NaBr are 35,363 J mol^{-1} and 225.2 J mol^{-1} K^{-1}.[19]

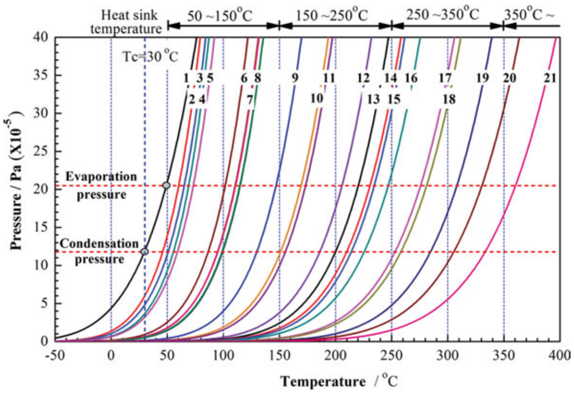

Figure 5. Equilibrium lines of metal chloride/bromine-ammonia in the Clapeyron diagram.

1-NH_3; 2-$PbCl_2$ (8/3.25); 3-NaBr (5.25/0); 4-$BaCl_2$ (8/0); 5-$PbBr_2$ (5.5/3); 6-$CaCl_2$ (8/4); 7-$SrCl_2$ (8/1); 8-$CaCl_2$(4/2); 9-$SrBr_2$ (8/2); 10-$MnCl_2$(6/2); 11-$CaBr_2$ (6/2); 12-$FeCl_2$(6/2); 13-$MnBr_2$(6/2); 14-$CoCl_2$(6/2); 15-$MgCl_2$(6/2); 16-$FeBr_2$(6/2); 17-$CoBr_2$(6/2); 18-$NiCl_2$(6/2); 19-$MgBr_2$(6/2); 20-$NiBr_2$(6/2); 21-NiI_2(6/2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

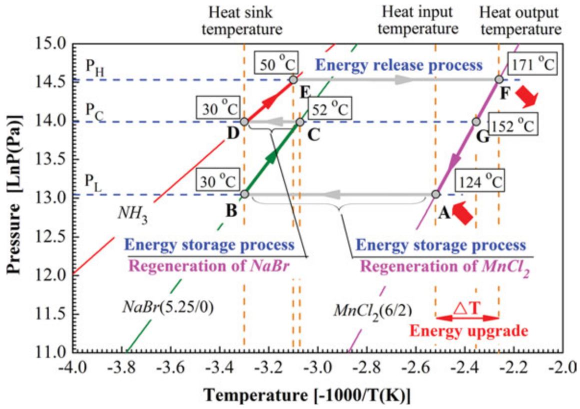

Figure 6. Theoretical Clapeyron diagram of the innovative solid-gas thermochemical sorption heat transformer using a group of sorption working pair $MnCl_2$-NaBr-NH_3.

TSHT-1Salt-L/G: G-D-E-F-G; TSHT-2Salts: A-B-C-G-A; TSHT-2Salts-L/G: A-B-C-D-E-F-A; energy storage process: A-B-C-D; energy upgrade process: D-E-F. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 shows the Clapeyron diagram of the innovative solid-gas thermochemical sorption heat transformer using a group of sorption working pair $MnCl_2$-NaBr-NH_3. The solid-gas and liquid-vapor equilibrium lines are calculated from the Clausius–Clapeyron equation, expressed as

$$Ln\left(\frac{P_{\mathrm{eq}}}{P^{o}}\right) = -\frac{\Delta H_{\mathrm{R}}}{R_0 T_{\mathrm{eq}}} + \frac{\Delta S}{R_0} \tag{3}$$

During energy storage phase of low-grade thermal energy using thermochemical pressure-reducing desorption process

$$\begin{cases} \mathrm{MnCl_2 \cdot 6NH_3} + \Delta H_{\mathrm{PRS}} \rightarrow \mathrm{MnCl_2 \cdot 2NH_3 + 4NH_3} \\ \mathrm{NaBr + 5.25NH_3 \rightarrow NaBr \cdot 5.25NH_3} + \Delta H_{\mathrm{SRS}} \end{cases} \tag{4}$$

$$\begin{cases} \mathrm{NaBr \cdot 5.25NH_3} + \Delta H_{\mathrm{SRS}} \rightarrow \mathrm{NaBr + 5.25NH_3} \\ \mathrm{NH_3(gas) \rightarrow NH_3(liq)} + \Delta H_{\mathrm{cond}} \end{cases} \tag{5}$$

During energy release phase of low-grade thermal energy using thermochemical temperature-lift adsorption process

$$\begin{cases} \mathrm{MnCl_2 \cdot 2NH_3 + 4NH_3 \rightarrow MnCl_2 \cdot 6NH_3} + \Delta H_{\mathrm{PRS}} \\ \mathrm{NH_3(liq)} + \Delta \mathrm{H_{evap}} \rightarrow \mathrm{NH_3(gas)} \end{cases} \tag{6}$$

The working process is constrained by three levels of pressure: low pressure (P_{L}) of the decomposition reaction phase of PRS during the first stage of energy storage process, condensation pressure (P_{c}) of the decomposition reaction phase of SRS during the second stage of energy storage process, and high pressure (P_{H}) of the synthesis reaction phase of PRS during energy release process.

For the thermochemical sorption heat transformer based on pressure-reducing desorption process and temperature-lift adsorption process (TSHT-2Salts-L/G), a pressure-reducing desorption method is introduced to lower heat input temperature during energy storage phase (A-B-C-D). At the heat sink temperature of 30°C, the PRS ($MnCl_2$) is heated by low-grade thermal energy at a heat input temperature of 124°C to desorb the refrigerant to the SRS (NaBr), and then the SRS is heated at a temperature of 52°C to desorb the refrigerant to the condenser. During energy upgrade phase (D-E-F), a temperature-lift adsorption method is used to upgrade the stored thermal energy. The refrigerant is first heated from the condensation temperature of 30°C to a higher-evaporation temperature of 50°C, and then it evaporates at a high pressure P_{H} and flows to the PRS reactor to react with $MnCl_2$. The synthesis reaction heat released by $MnCl_2$ is used to produce thermal energy at a high temperature of 171°C. In comparison with the heat input temperature during energy storage process, the heat output temperature is upgraded and it is equal to 171°C during energy release process (D-E-F), and the temperature upgrade of low-grade thermal energy is 47°C.

In comparison with the thermochemical sorption heat transformer based on temperature-lift adsorption process (TSHT-1Salt-L/G), the heat input temperature of $MnCl_2$ can be lowered from 152 to 124°C during energy storage process at the same heat sink temperature by using pressure-reducing desorption method in the proposed thermochemical sorption heat transformer based on pressure-reducing desorption process and temperature-lift adsorption process (TSHT-2Salts-L/G). Thus, it can enlarge the working temperature range of external low-grade thermal energy.

In comparison with the thermochemical sorption heat transformer based on pressure-reducing desorption process (TSHT-2Salts), the heat output temperature of $MnCl_2$ can be upgraded from 152 to 171°C during energy release process by using temperature-lift adsorption method in the proposed thermochemical sorption heat transformer based on pressure-reducing desorption process and temperature-lift adsorption process (TSHT-2Salts-L/G). Thus, it has a higher-temperature upgrade of low-grade thermal energy and thus can produce higher heat output temperature for end user.

Especially, due to the mismatch between the synthesis reaction rate of PRS and the decomposition reaction rate of SRS during energy release phase in TSHT-2Salts, the operating pressure is difficult to control and it usually has a strong fluctuation, which causes the decrease in heat output temperature. However, the operating pressure can be regulated by the evaporation pressure of refrigerant during energy release phase to overcome the aforementioned drawback in TSHT-2Salts-L/G. In addition, it can be seen in Figure 6 that the temperature magnitude of energy upgrade is as high as 47°C in TSHT-2Salts-L/G while it is 19 and 28°C in TSHT-1Salt-L/G and TSHT-2Salts, respectively, using the same sorption working pair.

It is noteworthy to mention that the group of sorption working pair $MnCl_2$-NaBr-NH_3 is only used as the example in Figure 6 to show that a low heat input temperature of 124°C can be upgraded to a high-heat output temperature of 171°C when the proposed target-oriented solid-gas thermochemical sorption heat transformer is introduced. Moreover, the lower-temperatures (e.g., only at 60–90°C) can also be upgraded to higher temperatures (e.g., higher than 100°C) when the same proposed method is used by utilizing appropriate sorption working pairs.

Performance Analysis of the Innovative Solid-Gas Thermochemical Sorption Heat Transformer

To evaluate the performance of the innovative solid-gas thermochemical sorption heat transformer, two parameters, energy efficiency and temperature magnitude of energy upgrade, are defined and used to analyze the working performance of different working modes of thermochemical sorption process for energy storage and energy upgrade of low-grade thermal energy.

The energy efficiency of low-grade thermal energy is defined as

$$\eta = \frac{\text{Useful heat production during energy release phase}}{\text{Total heat consumpation during energy storage phase}} = \frac{Q_{\text{out}}}{Q_{\text{in}}} \tag{7}$$

The temperature magnitude of energy upgrade of low-grade thermal energy is defined as

$$\Delta T = \text{Heat output temperature} - \text{Heat input temperature} = T_{\text{out}} - T_{\text{in}} \tag{8}$$

1. For the thermochemical sorption heat transformer based on temperature-lift adsorption process (TSHT-1Salt-L/G), the useful heat production during energy release phase and the total heat consumption during energy storage phase can be calculated by the following equations

$$Q_{\text{out}} = \underbrace{\Delta H_{\text{PRS}}}_{\text{Reaction heat of the PRS}} - \left(\underbrace{\int_{T_{\text{in}}}^{T_{\text{out}}} C_{\text{PRS}}^{\text{unloaded}} M_{PRS} dT}_{\text{Sensible heat of PRS}} + \underbrace{\int_{T_{\text{in}}}^{T_{\text{out}}} C_{\text{p-R}} M_{\text{PRS-R}} dT}_{\substack{\text{Sensible heat of the metallic part}\\ \text{of the PRS reactor}}} \right)_{\text{I}}^{\text{unloaded}} \tag{9}$$

where the first term in the right side of the equation is the reaction heat of the PRS during energy release phase; the second term is the sensible heat of the PRS; the last term is the sensible heat of the metallic part of the PRS reactor.

$$Q_{\text{in}} = \underbrace{\Delta H_{\text{PRS}} + \left(\int_{T_{\text{out}}}^{T_{\text{in}}} C_{\text{PRS}}^{\text{loaded}} M_{\text{PRS}} dT + \int_{T_{\text{out}}}^{T_{\text{in}}} C_{\text{p-R}} M_{\text{PRS-R}} dT \right)^{\text{loaded}}}_{\substack{\text{Total heat consumption of the PRS reactor}\\ \text{during the regeneration phase}}} + \underbrace{\Delta H_{\text{evap}} + \int_{T_{\text{c}}}^{T_{\text{he}}} C_{\text{p-NH}_3} M_{\text{NH}_3} dT + \int_{T_c}^{T_{he}} C_{\text{p-R}} M_{\text{NH}_3\text{-R}} dT}_{\substack{\text{Total heat input of the evaporator}\\ \text{during the temperature-lift adsorption phase}}} \tag{10}$$

where the first term in the right side of the equation is the total heat consumption of the PRS reactor during the regeneration phase of PRS, including the reaction heat and sensible heat of the PRS, and the sensible heat of the metallic part of the PRS reactor; the second term is the total heat input of the evaporator during the temperature-lift adsorption phase, including the evaporation heat and sensible heat of NH_3, and the sensible heat of the metallic part of evaporator.

2. For the thermochemical sorption heat transformer based on pressure-reducing desorption process (TSHT-2Salts), the useful heat production during energy release phase and the total heat consumption during energy storage phase can be calculated by the following equations

$$Q_{\text{out}} = \underbrace{\Delta H_{\text{PRS}}}_{\text{Reaction heat of the PRS}} - \left(\underbrace{\int_{T_{\text{in}}}^{T_{\text{out}}} C_{\text{PRS}}^{\text{unloaded}} M_{\text{PRS}} dT}_{\text{Sensible heat of the PRS}} + \underbrace{\int_{T_{\text{in}}}^{T_{\text{out}}} C_{\text{p-R}} M_{\text{PRS-R}} dT}_{\substack{\text{Sensible heat of the metallic part}\\ \text{of the PRS reactor}}} \right)_{\text{II}}^{\text{unloaded}} \tag{11}$$

where the first term in the right side of the equation is the reaction heat of the PRS during energy release phase; the second term is the sensible heat of the PRS; the last term is the sensible heat of the metallic part of the PRS reactor.

$$Q_{\text{in}} = \underbrace{\Delta H_{\text{PRS}} + \left(\int_{T_{\text{out}}}^{T_{\text{in}}} C_{\text{PRS}}^{\text{loaded}} M_{\text{PRS}} dT - \int_{T_{\text{out}}}^{T_{\text{in}}} C_{\text{p-R}} M_{\text{PRS-R}} dT \right)^{\text{loaded}}}_{\substack{\text{Total heat consumpation of the PRS reactor}\\ \text{during the pressure-reducing regeneration phase}}} + \underbrace{\Delta H_{\text{SRS}} + \left(\int_{T_{\text{a}}}^{T_{\text{d}}} C_{\text{SRS}}^{\text{loaded}} M_{\text{SRS}} dT + \int_{T_{\text{a}}}^{T_{\text{d}}} C_{\text{p-R}} M_{\text{SRS-R}} dT \right)^{\text{loaded}}}_{\substack{\text{Total heat consumpation of the SRS reactor}\\ \text{during the regeneration phase}}}$$

where the first term in the right side of the equation is the total heat consumption of the PRS reactor during the pressure-reducing desorption phase, including the reaction heat and sensible heat of the PRS, and the sensible heat of the metallic part of the PRS reactor; the second term is the total heat consumption of the SRS reactor during the regeneration phase, including the reaction heat and sensible heat of the SRS, and the sensible heat of the metallic part of the SRS reactor.

3. For the thermochemical sorption heat transformer based on pressure-reducing desorption process and temperature-lift adsorption process (TSHT-2Salts-L/G), the useful heat production during energy release phase and the total heat consumption during energy storage phase can be calculated by the following equations

$$Q_{\text{out}} = \underbrace{\Delta H_{\text{PRS}}}_{\text{Reaction heat of the PRS}} - \left(\underbrace{\int_{T_{\text{in}}}^{T_{\text{out}}} C_{\text{PRS}}^{\text{unloaded}} M_{\text{PRS}} dT}_{\text{Sensible heat of the PRS}} + \underbrace{\int_{T_{\text{in}}}^{T_{\text{out}}} C_{\text{p-R}} M_{\text{PRS-R}} dT}_{\substack{\text{Sensible heat of the metallic part} \\ \text{of the PRS reactor}}} \right)_{\text{III}}^{\text{unloaded}}$$

where the first term in the right side of the equation is the reaction heat of the PRS during energy release phase; the second term is the sensible heat of the PRS; the last term is the sensible heat of the metallic part of the PRS reactor.

$$Q_{\text{in}} = \underbrace{\Delta H_{\text{PRS}} + \left(\int_{T_{\text{out}}}^{T_{\text{in}}} C_{PRS}^{\text{loaded}} M_{\text{PRS}} dT + \int_{T_{\text{out}}}^{T_{\text{in}}} C_{\text{p-R}} M_{\text{PRS-R}} dT \right)^{\text{loaded}}}_{\substack{\text{Total heat consumpation of the PRS reactor} \\ \text{during the pressure-reducing regeneration phase}}} + \underbrace{\Delta H_{\text{SRS}} + \left(\int_{T_{\text{a}}}^{T_{\text{d}}} C_{\text{SRS}}^{\text{loaded}} M_{\text{SRS}} dT + \int_{T_{\text{a}}}^{T_{\text{d}}} C_{\text{p-R}} M_{\text{SRS-R}} dT \right)^{\text{loaded}}}_{\substack{\text{Total heat consumpation of the SRS reactor} \\ \text{during the regeneration phase}}}$$
$$+ \underbrace{\Delta H_{\text{evap}} + \int_{T_{\text{c}}}^{T_{\text{he}}} C_{\text{NH}_3} M_{\text{NH}_3} dT + \int_{T_{\text{c}}}^{T_{\text{he}}} C_{\text{p-R}} M_{\text{NH}_3\text{-R}} dT}_{\substack{\text{Total heat input of the evaporator} \\ \text{during the temperature-lift adsorption phase}}} \qquad (14)$$

where the first term in the right side of the equation is the total heat consumption of the PRS reactor during the pressure-reducing desorption phase, including the reaction heat and sensible heat of the PRS, and the sensible heat of the metallic part of the PRS reactor; the second term is the total heat consumption of the SRS reactor during the regeneration phase, including the reaction heat and sensible heat of the SRS, and the sensible heat of the metallic part of the SRS reactor; the third term is the total heat input of the evaporator during the temperature-lift adsorption phase, including the evaporation heat and sensible heat of NH_3, and the sensible heat of the metallic part of evaporator.

Performance comparison in the energy efficiency and temperature upgrade of low-grade thermal energy using different thermochemical sorption heat transformer techniques

Figure 7 shows the performance comparison in the energy efficiency and temperature upgrade of low-grade thermal energy based on the different thermochemical sorption heat transformer techniques using a group of sorption working pair $MnCl_2$-NaBr-NH_3. The case of TSHT-1Salt-L/G is the energy upgrade using thermochemical sorption heat transformer based on temperature-lift adsorption process, the case of TSHT-2Salts is the energy upgrade using thermochemical sorption heat transformer based on pressure-reducing desorption process, and the case of TSHT-2Salts-L/G is the energy upgrade using thermochemical sorption heat transformer based on pressure-reducing desorption process and temperature-lift adsorption process.

For the thermochemical sorption heat transformer based on temperature-lift adsorption process (TSHT-1Salt-L/G), the energy efficiency is 0.67, and the low-grade thermal energy

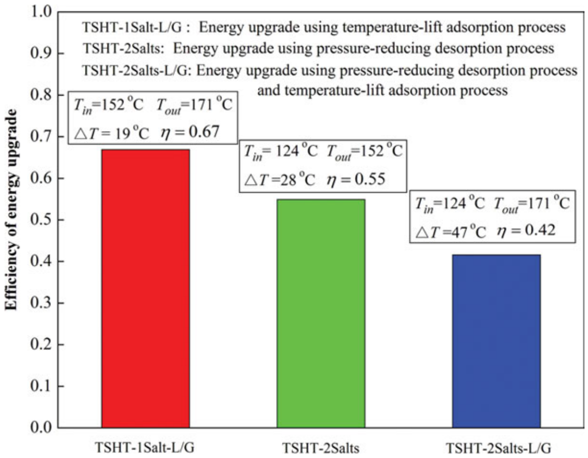

Figure 7. Performance comparison in the energy efficiency and temperature upgrade of low-grade thermal energy based on the thermochemical sorption heat transformer using sorption working pair $MnCl_2$-NaBr-NH_3.

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

can be upgraded from 152 to 171°C, thus, the temperature upgrade is 19°C. For the thermochemical sorption heat transformer based on pressure-reducing desorption process (TSHT-2Salts), the energy efficiency is 0.55, and the low-grade thermal energy can be upgraded from 124 to 152°C, thus, the temperature upgrade is 28°C. For the thermochemical sorption heat transformer based on pressure-reducing desorption process and temperature-lift adsorption process (TSHT-2Salts-L/G), the energy efficiency is 0.47, and the low-grade thermal energy can be upgraded from 124 to 171°C, thus, the temperature upgrade is 47°C. It can be seen that TSHT-1Salt-L/G has the highest energy efficiency and the lowest temperature upgrade of low-grade thermal energy, while TSHT-2Salts-L/G has the highest temperature upgrade and the lowest energy efficiency of low-grade thermal energy.

The difference in the energy efficiency of low-grade thermal energy can be attributed to the different heat consumption during energy storage phase and the sensible heat of heat exchanger during energy release phase. In comparison with the thermochemical sorption heat transformer using TSHT-1Salt-L/G, the heat input of the SRS during energy storage phase is the additional heat consumption in the thermochemical sorption heat transformer using TSHT-2Salts-L/G due to the realization of pressure-reducing desorption process. When compared with the thermochemical sorption heat transformer using TSHT-2Salts, the heat input of the evaporator during energy release phase is the additional consumption in TSHT-2Salts-L/G due to the realization of temperature-lift adsorption process. Thus, the thermochemical sorption heat transformer using TSHT-2Salts-L/G has the lowest energy efficiency among these thermochemical sorption heat transformer techniques because of the aforementioned additional heat consumption.

It can be concluded that the energy efficiency decreases with the increase in the temperature upgrade of low-grade thermal energy for three different thermochemical sorption heat transformer techniques. The order of energy efficiency of low-grade thermal energy is as follows: TSHT-1Salt-L/G > TSHT-2Salts > TSHT-2Salts-L/G. The order of temperature upgrade of low-grade thermal energy is as follows: TSHT-2Salts-L/G > TSHT-2Salts > TSHT-1Salt-L/G.

Effect of reactor thermal capacity on the energy efficiency of low-grade thermal energy using thermochemical sorption heat transformer

A parameter R, defined as the mass ratio of the metallic part of heat exchanger (including vessels, tubes, fins) to the reactive salt in solid-gas reactor, is used to assess the effect of reactor thermal capacity on the energy efficiency of low-grade thermal energy. Different R means the different mass percentage of metal in the total mass of a reactor, thus, the value of R reflects the optimization design of the solid-gas reactor. The variation of the energy efficiency with different mass ratio R is shown Figure 8.

It can be seen that the mass ratio R has a negative influence on the system performance and the energy efficiency decreases as the mass ratio R increases. This is because high R means the increase in the heat consumption from external heat source during energy storage phase, which causes the decrease in the energy efficiency. For the three thermochemical sorption heat transformer techniques based on a group of sorption working pair $MnCl_2$-NaBr-NH_3, the decreasing magnitudes of energy efficiencies with the mass ratio R are different. As R increases from 0 to 20, the energy efficiency decreases by 9, 14, and 26 % for the thermochemical sorption heat transformer using TSHT-1Salt-L/G, TSHT-2Salts, and TSHT-2Salts-L/G, respectively. Moreover, the thermochemical sorption heat transformer using TSHT-2Salts-L/G has the highest decreasing rate of the energy efficiency as shown in Figure 8. This can be attributed to the fact that both sensible heat consumptions of the PRS and SRS reactors are influenced by the thermal capacity of metal during energy storage phase. It indicates that the reactor thermal capacity has a more significant influence on the working performance of the thermochemical sorption heat transformer using TSHT-2Salts-L/G when compared with the thermochemical sorption heat transformer using TSHT-1Salt-L/G and TSHT-2Salts.

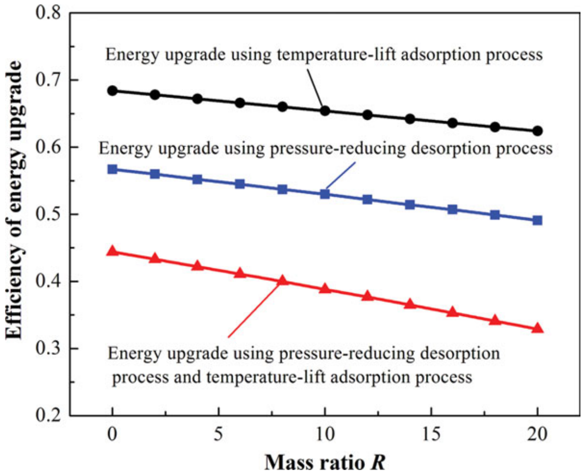

Figure 8. Effect of reactor thermal capacity on the energy efficiency of low-grade thermal energy using thermochemical sorption heat transformer.

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

However, in comparison with the strong influence of reactor thermal capacity on the working performance of solid-gas thermochemical sorption refrigeration system,[20] the influence of reactor thermal capacity on the energy efficiency of solid-gas thermochemical sorption heat transformer becomes weak. This is because the sensible heat of metallic part of reactor plays a heat recovery function during the interchange phases of energy storage and energy release, and the amount of thermal energy can be regarded as the sensible heat storage using metal materials. For example, a proportion of energy must be consumed to heat the reactor from T_{in} to T_{out} before start to produce useful thermal energy during energy release phase in the three thermochemical sorption heat transformer techniques. In this case, the heat consumption of the metallic part of reactor plays a negative effect. However, when the working mode is interchanged from energy release to energy storage, this part of energy can be recovered to supply the decomposition reaction heat when reactor is cooled down from T_{out} to T_{in}. In this case, the sensible heat of the metallic part of reactor plays a positive effect and the total heat consumption from external heat source reduces. However, it is noteworthy to mention that although the influence of metallic thermal capacity of reactor on the energy efficiency is relatively weak for the solid-gas thermochemical sorption heat transformer, but it has a strong influence on the amount of thermal energy supply for end user. Usually, for most solid-

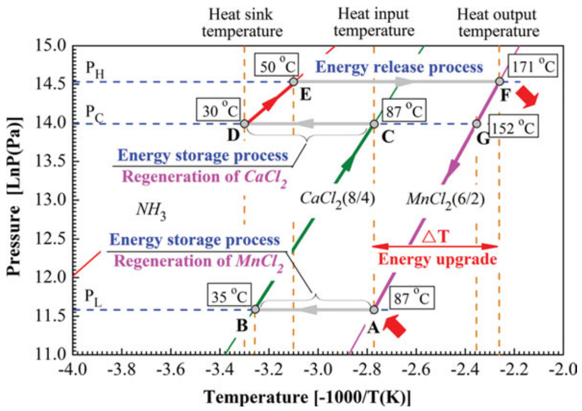

Figure 9. Theoretical Clapeyron diagram of the innovative solid-gas thermochemical sorption heat transformer using a group of sorption working pair $MnCl_2$-$CaCl_2$-NH_3.

TSHT-1Salt-L/G: G-D-E-F-G; TSHT-2Salts: A-B-C-G-A; TSHT-2Salts-L/G: A-B-C-D-E-F-A; energy storage process: A-B-C-D; energy upgrade process: D-E-F. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

gas thermochemical sorption systems with optimized design, the mass ratio (R) between the metallic part of the reactor and the reactive salt is about 5.

The Target-Oriented Characteristics of the Proposed Innovative Solid-Gas Thermochemical Sorption Heat Transformer

Thermodynamic analysis of the target-oriented characteristics of the proposed thermochemical sorption heat transformer

In comparison with the conventional heat transformer technologies, the proposed innovative thermochemical sorption heat transformer has a distinct advantage of its target-oriented characteristics. The temperature magnitude of energy upgrade can be adjusted by choosing appropriate sorption working pairs in the proposed target-oriented solid-gas thermochemical sorption heat transformer, in which the heat input temperature from external available heat source and the heat output temperature for end user are combined as the target-oriented requirement. The heat input temperature is adjusted by using pressure-reducing desorption method during energy storage phase and the heat output temperature is adjusted by using temperature-lift adsorption method during energy release phase.

Figures 9 and 10 show the working principles of the innovative target-oriented thermochemical sorption heat transformer using sorption working pairs of $MnCl_2$-$CaCl_2$-NH_3 and $NiCl_2$-$SrBr_2$-NH_3, respectively, in which $MnCl_2$ and $NiCl_2$ are used as the PRS, $CaCl_2$ and $SrBr_2$ are used as the SRS, whereas NH_3 is the refrigerant.

Assuming that the heat out temperature is kept equivalent for a given end user, and the decrease in the heat input temperature from external low-grade heat sources is used as the target-oriented requirement, in this case, the PRS should be kept same while the SRS should be changed. For example, sodium bromine (in Figure 6) can be replaced with calcium chloride (in Figure 9) to widen the working temperature range of available low-grade heat sources, in which $CaCl_2$ is used as the SRS to lower the regeneration temperature of $MnCl_2$ during energy storage process.

During energy storage phase of low-grade thermal energy using thermochemical pressure-reducing desorption process

$$\begin{cases} MnCl_2 \cdot 6NH_3 + \Delta H_{PRS} \rightarrow MnCl_2 \cdot 2NH_3 + 4NH_3 \\ CaCl_2 \cdot 4NH_3 + 4NH_3 \rightarrow CaCl_2 \cdot 8NH_3 + \Delta H_{SRS} \end{cases} \tag{15}$$

$$\begin{cases} CaCl_2 \cdot 8NH_3 + \Delta H_{SRS} \rightarrow CaCl_2 \cdot 4NH_3 + 4NH_3 \\ NH_3(gas) \rightarrow NH_3(liq) + \Delta H_{cond} \end{cases} \tag{16}$$

During energy release phase of low-grade thermal energy using thermochemical temperature-lift adsorption process

$$\begin{cases} MnCl_2 \cdot 2NH_3 + 4NH_3 \rightarrow MnCl_2 \cdot 6NH_3 + \Delta H_{PRS} \\ NH_3(liq) + \Delta H_{evap} \rightarrow NH_3(gas) \end{cases} \tag{17}$$

At the same heat sink temperature of 30°C and heat output temperature of 171°C, it can be seen that the heat input temperature during energy storage phase is lowered from 124°C in Figure 6 to 87°C in Figure 9 when the sorption pair of $MnCl_2$-NaBr-NH_3 is replaced by the sorption pair of $MnCl_2$-$CaCl_2$-NH_3. Thus, the working temperature range of available low-grade heat sources can be effectively extended. Moreover, the temperature magnitude of energy upgrade can be further upgrade to 84°C in the thermochemical sorption heat transformer using TSHT-2Salts-L/G.

If the increase in the heat output temperature for end user and temperature magnitude of energy upgrade are used as the target-oriented requirement, both PRS and SRS should be replaced by other reactive salts. For example, a group of sorption working pair $NiCl_2$ -$SrBr_2$-NH_3 is used as shown in Figure 10.

During energy storage phase of low-grade thermal energy using thermochemical pressure-reducing desorption process

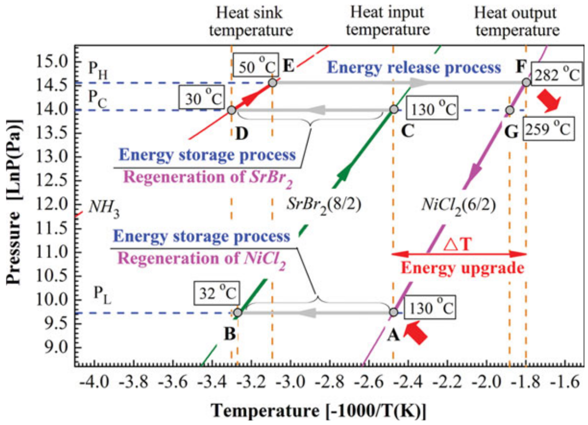

Figure 10. Theoretical Clapeyron diagram of the innovative solid-gas thermochemical sorption heat transformer using a group of sorption working pair $NiCl_2$-$SrBr_2$-NH_3.

TSHT-1Salt-L/G: G-D-E-F-G; TSHT-2Salts: A-B-C-G-A; TSHT-2Salts-L/G: A-B-C-D-E-F-A; energy storage process: A-B-C-D; energy upgrade process: D-E-F. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 1. Mass of Reactive Salt necessary to Desorb/Adsorb 1 kg of NH_3 in the Solid-Gas Thermochemical Sorption Heat Transformer

Thermochemical sorption working pair for energy upgrade	Secondary reactive salt (SRS)	Primary reactive salt (PRS)
Sorption working pair of $MnCl_2$-NaBr-NH_3	Mass of NaBr 1.15 kg	Mass of $MnCl_2 \cdot 2NH_3$ 2.35 kg
Sorption working pair of $MnCl_2$-$CaCl_2$-NH_3	Mass of $CaCl_2 \cdot 4NH_3$ 2.63 kg	Mass of $MnCl_2 \cdot 2NH_3$ 2.35 kg
Sorption working pair of $NiCl_2$-$SrBr_2$-NH_3	Mass of $SrBr_2 \cdot 2NH_3$ 2.76 kg	Mass of $NiCl_2 \cdot 2NH_3$ 2.40 kg

$$\begin{cases} NiCl_2 \cdot 6NH_3 + \Delta H_{PRS} \rightarrow NiCl_2 \cdot 2NH_3 + 4NH_3 \\ SrBr_2 \cdot 2NH_3 + 6NH_3 \rightarrow SrBr \cdot 8NH_3 + \Delta H_{SRS} \end{cases} \tag{18}$$

$$\begin{cases} SrBr \cdot 8NH_3 + \Delta H_{SRS} \rightarrow SrBr \cdot 2NH_3 + 6NH_3 \\ NH_3(gas) \rightarrow \ NH_3(liq) + \Delta H_{cond} \end{cases} \tag{19}$$

During energy release phase of low-grade thermal energy using thermochemical temperature-lift adsorption process

$$\begin{cases} NiCl_2 \cdot 2NH_3 + 4NH_3 \rightarrow NiCl_2 \cdot 6NH_3 + \Delta H_{PRS} \\ NH_3(liq) + \Delta H_{evp} \rightarrow NH_3(gas) \end{cases} \tag{20}$$

Figure 10 shows that a higher heat out temperature and a further magnitude of energy upgrade can be achieved at the same heat sink temperature by using sorption working pair $NiCl_2$-$SrBr_2$-NH_3 in comparison with the case in Figure 6. The heat input temperature is 130°C during energy storage phase of A-B-C-D using pressure-reducing desorption process, and the heat output temperature is 282°C during energy release process of D-E-F using temperature-lift adsorption process. The temperature magnitude of energy upgrade is as high as 152°C. Thus, the heat output temperature and temperature magnitude of energy upgrade are effectively improved.

Performance comparison in the energy efficiency and temperature upgrade of low-grade thermal energy using different sorption working pair

Combining the Eqs. 7 and 14 and the Clapeyron diagrams, the working performance of the energy efficiency and the temperature magnitude of energy upgrade are analyzed and compared for the different thermochemical sorption heat transformer techniques. The same cycled mass of ammonia was assumed to determine the mass of each metallic salt complex required in the different thermochemical sorption working pairs for energy upgrade as shown in Table 1.

Performance comparison in the energy efficiency and temperature magnitude of energy upgrade of low-grade thermal energy using different sorption working pairs is shown in Table 2. For different sorption working pairs, the energy efficiency decreases with increasing the temperature magnitude of energy upgrade of low-grade thermal energy. For a given sorption working pair in different heat transformer techniques, the highest energy efficiency is obtained using TSHT-1Salt-L/G, while the highest temperature magnitude of energy upgrade is obtained when the TSHT-2Salts-L/G is used.

Although PRS and heat output temperatures are same for the two sorption working pairs of $MnCl_2$-$CaCl_2$-NH_3 and $MnCl_2$-NaBr-NH_3, it is found that the former sorption working pair has higher-temperature magnitude of energy upgrade when compared with the latter sorption working pair. For example, as the same techniques of TSHT-2Salts-L/G are used, the temperature magnitude of energy upgrade is 84°C for the sorption working pair $MnCl_2$-$CaCl_2$-NH_3, while it becomes 47°C for the sorption working pair $MnCl_2$-NaBr-NH_3. This is because the heat input temperature during energy storage phase in the former working pair is much lower than that in the latter working pair when NaBr is replaced by $CaCl_2$ using as SRS.

However, $MnCl_2$-$CaCl_2$-NH_3 working pair has lower-energy efficiency than *$MnCl_2$-NaBr-NH_3* working pair. For example, in the case of TSHT-2Salts-L/G, the energy efficiency is 0.42 in the former sorption working pair, whereas it is 0.36 in the latter sorption working pair. This is because the sensible heat consumptions of SRS during energy storage phase are different in the two sorption work pairs. As $CaCl_2$ is used as the SRS, it should be heated from 30 to 87°C, and the heating temperature difference is 57°C. When NaBr is used as the SRS, the heating temperature difference becomes 22°C as the SRS is heated from 30 to 52°C. Thus, the sensible heat consumption of SRS in the former sorption working pair is higher than that in the latter sorption working pair. Therefore, the high-heat consumption causes the decrease in the energy efficiency.

For the heat transformer technique of TSHT-1Salt-L/G using two sorption working pairs of $MnCl_2$-$CaCl_2$-NH_3 and $MnCl_2$-NaBr-NH_3, although the second reactive salts are different, the energy efficiency and temperature magnitude of energy upgrade are still same. This is because the energy efficiency and the temperature magnitude of energy upgrade are only dependent on the PRS, and they are independent on

Table 2. Performance Analysis of Energy Upgrade of Low-Grade Thermal Energy Based on Solid-Gas Thermochemical Sorption Heat Transformer

Sorption working pairs for energy upgrade	Energy upgrade technology	Energy efficiency, η	Heat input temperature, T_{in} (°C)	Heat output temperature, T_{out} (°C)	Magnitude of energy upgrade, ΔT (°C)
$MnCl_2$-NaBr-NH_3	TSHT-1Salt-L/G	0.67	152	171	19
	TSHT-2Salts	0.55	124	152	28
	TSHT-2Salts-L/G	0.42	124	171	47
$MnCl_2$-$CaCl_2$-NH_3	TSHT-1Salt-L/G	0.67	152	171	19
	TSHT-2Salts	0.46	87	152	65
	TSHT-2Salts-L/G	0.36	87	171	84
$NiCl_2$-$SrBr_2$-NH_3	TSHT-1Salt-L/G	0.72	259	282	23
	TSHT-2Salts	0.43	130	259	129
	TSHT-2Salts-L/G	0.34	130	282	152

TSHT-1Salt-L/G: energy upgrade using temperature-lift adsorption process.
TSHT-2Salts: energy upgrade using pressure-reducing desorption adsorption process.
TSHT-2Salts-L/G: energy upgrade using pressure-reducing desorption process and temperature-lift adsorption process.

Table 3. Performance Analysis of the Energy Density using Thermochemical Sorption Working Pairs at Different Operating Temperatures

Reactive salt	Reaction enthalpy ΔH ($J\ mol^{-1}$)	Reaction entropy ΔS ($J\ mol^{-1}\ K^{-1}$)	Reaction coefficient m	Reaction coefficient n	Molar mass ($g\ mol^{-1}$)	Driving equilibrium temperature (°C)	Energy density ($kJ\ kg^{-1}$)
NH_4Cl 3/0	29,433	207.9	3	0	53.4	48	1654
$PbCl_2$ 8/3.25	34,317	223.6	4.75	3.25	278	47	586
NaBr 5.25/0	35,363	225.2	5.25	0	102.9	51	1804
$BaCl_2$ 8/0	38,250	232.4	8	0	208.2	56	1470
LiCl 4/3	36,828	224.6	1	3	42.3	67	871
$CaCl_2$ 8/4	41,013	230.1	4	4	110.8	87	1481
NaI 4.5/0	39,339	224.5	4.5	0	149.9	90	1181
$BaBr_2$ 8/4	41,850	229.8	4	4	297.1	95	563
$SrCl_2$ 8/1	41,432	228.6	7	1	158.4	96	1831
$CaCl_2$ 4/2	42,269	229.7	2	2	110.8	99	763
$SrBr_2$ 8/2	45,617	229.3	6	2	247.4	130	1106
$MnCl_2$ 6/2	47,416	227.9	4	2	125.7	152	1509
$CaBr_2$ 6/2	48,965	230.4	4	2	199.8	156	980
$FeCl_2$ 6/2	51,266	227.8	4	2	126.6	186	1620
$MnBr_2$ 6/2	53,066	228.3	4	2	214.7	200	989
$CoCl_2$ 6/2	53,987	227.9	4	2	94.3	210	2290
$MgCl_2$ 6/2	55,661	230.4	4	2	95.1	214	2341
$FeBr_2$ 6/2	55,828	228.1	4	2	215.6	226	1036
CaI_2 6/2	58,590	231.0	4	2	293.8	237	798
$CoBr_2$ 6/2	58,590	227.5	4	2	218.7	253	1072
$NiCl_2$ 6/2	59,218	227.6	4	2	129.5	259	1829
MnI_2 6/2	59,301	227.4	4	2	308.7	260	768
FeI_2 6/2	60,683	227.5	4	2	309.6	272	784
$MgBr_2$ 6/2	63,612	230.2	4	2	184.1	285	1382
$NiBr_2$ 6/2	64,240	227.2	4	2	218.5	306	1176
NiI_2 6/2	65,453	224.1	4	2	312.5	334	838

Reversible reaction: $\text{Sold} \cdot (n+m)NH_3 + \Delta H \leftrightarrow \text{Solid} \cdot nNH_3 + mNH_3(\text{gas})$.

Reaction enthalpy and entropy from the Ref. [19].

the SRS when only the temperature-lift adsorption technique is used in the TSHT-1Salt-L/G.

For three different heat transformer techniques of TSHT-1Salts-L/G, TSHT-2Salts, and TSHT-2Salts-L/G, the sorption working pair $NiCl_2$-$SrBr_2$-NH_3 has higher-temperature upgrade than the sorption working pair $MnCl_2$-$CaCl_2$-NH_3, but the former working pair has lower-energy efficiency than the latter working pair in the two cases of TSHT-2Salts and TSHT-2Salts-L/G. However, the energy efficiency of former working pair becomes higher than that of latter working pair in the other case of TSHT-1Salt-L/G. The reason can be explained as follows

$NiCl_2$ has higher-reaction enthalpy than $MnCl_2$, and thus the amount of heat production becomes higher during energy release phase. On the other hand, the heat consumptions of evaporator are same for the two different sorption working pairs during the temperature-lift adsorption process in the case of TSHT-1Salt-L/G. Thus, the heat consumption of the evaporator has a lower account for the total heat consumption in the sorption working pair $NiCl_2$-$SrBr_2$-NH_3 when compared with the sorption working pair $MnCl_2$-$CaCl_2$-NH_3, Therefore, the former working pair has higher-energy efficiency. However, when $SrBr_2$ is used as the SRS to perform pressure-reducing desorption process in the other two cases of TSHT-2Salts and TSHT-2Salts-L/G, the heat consumption of $SrBr_2$ is large higher than that of $CaCl_2$ during energy storage phase. Thus, the high-heat consumption decreases the energy efficiency in the former sorption working pair.

Performance analysis of the energy density using thermochemical sorption working pairs at different operating temperatures

For the reutilization of low-grade heat sources with different available temperatures, it is necessary to select suitable sorption working pairs to achieve energy storage and energy upgrade at different operating temperatures. For the proposed solid-gas thermochemical sorption heat transformer, the general principle for choosing the sorption working pair for the integrated energy storage and energy upgrade is suggested as follows: PRS should be first selected according to the heat output temperature for end user, and then SRS is selected according to the external available heat source temperature.

Performance analysis of the energy density using thermochemical sorption working pairs at different operating temperatures is shown in Table 3. The driving equilibrium temperature is calculated on the assumption that the heat sink temperature is 30°C. It can be seen that the reaction enthalpy

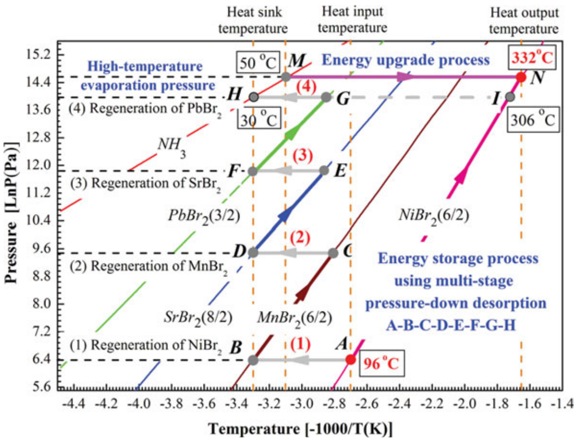

Figure 11. Operating principle of the advanced multi-stage innovative solid-gas thermochemical sorption heat transformer.

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

and entropy between reactive salts and ammonia are dissimilar for thermochemical sorption working pairs at different operating temperatures. Moreover, the amounts of ammonia adsorbed/desorbed by salts are also different. General speaking, these reactive salts with high-sorption capacity should be preferentially chosen as the energy upgrade materials to improve the energy density.

For most reactive salt for the integrated energy storage and energy upgrade, the energy density is higher than 800 kJ kg^{-1}, which is about 2–5 times than that obtained with latent heat storage method using phase change materials (PCM). Therefore, the higher-energy density is beneficial to reducing the volume size of energy storage equipment.

Especially, if external available heat source temperature is rather low or high-temperature magnitude of energy upgrade is required, advanced multistage thermochemical sorption heat transformer can also be developed by introducing the same proposed temperature-lift adsorption techniques and multistage pressure-reducing desorption.[21] In this case, a further decrease in the heat input temperature can be attained and a further increase in the heat output temperature can be achieved, thus, a higher-temperature magnitude of energy upgrade of low-grade thermal energy would be obtained. For example, heat input temperature of nickel bromine salt would become 96°C using the proposed multistage pressure-reducing desorption method and the temperature magnitude of energy upgrade would be as high as 236°C if the advanced thermochemical sorption heat transformer A-B-C-D-E-F-G-H-M-N is introduced as shown in Figure 11.

Conclusion

An innovative target-oriented solid-gas thermochemical sorption heat transformer is developed for the integrated energy storage and energy upgrade of low-grade thermal energy. The operating principle of the proposed thermochemical sorption heat transformer is based on the reversible solid-gas chemical reaction between a sorption material and a gas, whereby thermal energy is stored in form of chemical bonds resulting from thermochemical sorption process. The working performance of the proposed thermochemical sorption heat transformer is analyzed, and the main results obtained are as follows

1. Theoretical results show that the innovative thermochemical sorption heat transformer is an efficient method for the integrated energy storage and energy upgrade of low-grade thermal energy. Moreover, the proposed thermochemical sorption heat transformer has distinct advantages of its target-oriented characteristics in comparison with the conventional thermochemical sorption heat transformer, and it can give the flexibility of deciding the temperature magnitude of energy upgrade of low-grade thermal energy.
2. Energy efficiency decreases with increasing the temperature upgrade of low-grade thermal energy and the reactor thermal capacity for different thermochemical sorption heat transformer techniques. The order of energy efficiency is as follows: TSHT-1Salt-L/G > TSHT-2Salts > TSHT-2Salts-L/G, and the order of temperature upgrade is as follows: TSHT-2Salts-L/G > TSHT-2Salts > TSHT-1Salt-L/G.
3. For the proposed target-oriented thermochemical sorption heat transformer, the temperature magnitude of energy upgrade of low-grade thermal energy can be controlled by choosing appropriate sorption working pairs, in which the heat input temperature from external available heat source and the heat output temperature for end user are combined as the target-oriented requirement. The heat input temperature can be adjusted by using pressure-reducing desorption process during energy storage phase and the heat output temperature can be adjusted by using temperature-lift adsorption process during energy release phase.
4. Different temperature magnitudes of energy upgrade of low-grade thermal energy can be achieved in the target-oriented thermochemical sorption heat transformer. The working temperature of low-grade thermal energy can be upgraded from 87 to 171°C using a group of sorption working pair $MnCl_2$-$CaCl_2$-NH_3, and it would be upgraded from 130 to 282°C when a group of sorption working pair $NiCl_2$-$SrBr_2$-NH_3 is employed. The proposed innovative thermochemical sorption heat transformer can provide a promising method for the high-efficient utilization of low-grade thermal energy.

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Notation

COP = coefficient of performance
$C_{p\text{-}HTS}$ = specific heat of high-temperature reactant (kJ kg^{-1} $°C^{-1}$)
$C_{p\text{-}LTS}$ = specific heat of low-temperature reactant (kJ kg^{-1} $°C^{-1}$)
$C_{p\text{-}R}$ = specific heat of metallic reactor(kJ kg^{-1} $°C^{-1}$)
$H_c(T_c)$ = enthalpy of refrigerant at condensation temperature (kJ mol^{-1})
$H_e(T_e$ = enthalpy of refrigerant at evaporation temperature (kJ mol^{-1})
M_{HTS} = molar mass of high-temperature reactant (kg mol^{-1})
M_{LTS} = molar mass of low-temperature reactant (kg mol^{-1})
m_{HR} = mass of high-temperature metallic reactor (kg)
m_{LR} = mass of low-temperature metallic reactor (kg)
P_c = condensation pressure (Pa)
P_e = evaporation pressure (Pa)
$P_{eq}(T_{eq})$ = equilibrium pressure (Pa)
P_L = resorption pressure (Pa)
Q = thermal energy (kJ)
$Q_{ads\text{-}coding}$ = cold production during the adsorption process (kJ)
$Q_{des\text{-}L}$ = desorption heat of low-temperature salt (kJ)
$Q_{heating}$ = total heat consumption during regeneration process (kJ)
$Q_{res\text{-}cooling}$ = cold production during the resorption process (kJ)
R = mass ratio of the metallic part of the reactor to the reactive salt
R_0 = universal gas constant (kJ mol^{-1} $°C^{-1}$)
T_a = adsorption temperature of reactive salt (°C)
T_c = heat sink temperature (°C)
T_d = desorption temperature of reactive salt (°C)
$T_{eq}(P_{eq})$ = equilibrium temperature (°C)
T_{rec} = internal heat recovery temperature (°C)
$T_{des\text{-}L}$ = refrigeration temperature of low-temperature salt (°C)
X = global conversion of chemical reaction

Greek letters

ΔH = reaction enthalpy of salt (kJ mol^{-1})
ΔH_{cond} = condensation enthalpy of refrigerant (kJ mol^{-1})
ΔH_R = enthalpy of transformation (kJ mol^{-1})
ΔH_{evap} = vaporization enthalpy of refrigerant (kJ mol^{-1})
ΔS = entropy of transformation (kJ $mol^{-1}°C^{-1}$)
n = number of moles of reactive salt
γ = ideal number of moles of refrigerant consumed per mole of reactive salt

Subscripts

ads = adsorption
cond = condensation

des = desorption
evap = evaporation
HTF = heat transfer fluid
HTS = high-temperature salt
LTS = low-temperature salt
res = resorption
loaded = loaded state
TSHT-1Salt-L/G = thermochemical sorption heat transformer based on temperature-lift adsorption process
TSHT-2Salts = thermochemical sorption heat transformer based on pressure-reducing desorption process
TSHT-2Salts-L/G = thermochemical sorption heat transformer based on pressure-reducing desorption process and temperature-lift adsorption process

Literature Cited

1. Agarwal AK. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. *Prog Energy Combust Sci*. 2007; 33:233–271.
2. Wang RZ, Oliveira RG. Adsorption refrigeration—an efficient way to make good use of waste heat and solar energy. *Prog Energy Combust Sci*. 2006;32:424–458.
3. Spoelstra S, Haije WG, Dijkstra JW. Techno-economic feasibility of high- temperature high-lift chemical heat pumps for upgrading industrial waste heat. *Appl Therm Eng*. 2002;22:1619–1630.
4. Neal E. Heat pumps-Applications for heating conservation and heat recovery. *Prog Energy Combust Sci*. 1983;9:179–197.
5. Kurem E, Horuz I. A comparison between ammonia-water and water-lithium bromide solutions in absorption heat transformers. *Int Commun Heat Mass Transfer*. 2001;28:427–438.
6. Haije WG, Veldhuis JBJ, Smeding SF, Grisel RJH. Solid/vapour sorption heat transformer: design and performance. *Appl Therm Eng*. 2007;27:1371–1376.
7. Aristov YI. Optimal adsorbent for adsorptive heat transformers: dynamic considerations. *Int J Refrig*. 2009;32:675–686.
8. Yu YQ, Zhang P, Wu JY, Wang RZ. Energy upgrading by solid-gas reaction heat transformer: a critical review. *Renew Sustain Energy Rev*. 2008;12:1302–1324.
9. Meunier F. Solid sorption heat powered cycles for cooling and heat pumping applications. *Appl Therm Eng*. 1998;18:715–729.
10. Neveu P, Castaing J. Development of a numerical sizing tool for a solid-gas thermochemical transformer-impact of the microscopic process on the dynamic behaviour of a solid-gas reactor. *App Therm Eng*. 1997;17:501–518.
11. Lepinasse E, Goetz V, Crozat G. Modeling and experimental investigation of a new type of thermochemical transformer based on the coupling of two solid-gas reactions. *Chem Eng Process.* 1994;33:125–134.
12. Vasiliev LL, Mishkinis DA, Antukh AA. Resorption heat pump. *Appl Therm Eng*. 2004;24:1893–1903.
13. Neveu P, Castaiang J. Solid–gas chemical heat pumps: field of application and performance of the internal heat recovery process. *Heat Recovery Syst CHP*. 1993;13:233–251.
14. Wang C. Zhang P. Wang RZ. Investigation of solid-gas reaction heat transformer system with the consideration of multi-step reaction. *AIChE J*. 2008;54:2464–2478.
15. Wongsuwan W, Kumar S, Neveu P, Meunier F. A review of chemical heat pump technique and applications. *Appl Therm Eng*. 2001;21:1489–1519.
16. Spinner B. Ammonia-based thermochemical transformers. *Heat Recovery Syst CHP*. 1993;13:301–307.
17. Li TX, Wang RZ, Kiplagat JK, Wang LW. A conceptual design and performance analysis of a triple-effect sorption refrigeration system with internal heat recovery. *Chem Eng Sci*. 2009;64:3376–3384.
18. Neveu P, Castaing J. Solid-gas chemical heat pumps: field of application and performance of the internal heat recovery. *Heat Recovery Syst CHP*. 1993;13:233–251.
19. Berthiaud J. *Procédés à sorption solide/gaz pour le transport de chaleur et de froid à longue distance*. Doctor Dissertation. Perpignan, France: PROMES, 2007.
20. Li TX, Wang RZ, Oliveira RG, Wang LW. Performance analysis of an innovative multi-mode, multi-salt and multi-effect chemisorption refrigeration system. *AIChE J*. 2007;53:3222–3230.
21. Li TX, Wang RZ, Kiplagat JK, Chen H, Wang LW. A new target-oriented methodology of decreasing the regeneration temperature of solid-gas thermochemical sorption refrigeration system driven by low-grade thermal energy. *Int J Heat Mass Transfer*. 2011;54:4719–4729.

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