Korean J. Chem. Eng., **17**(2), 248-251 (2000)

SHORT COMMUNICATION

Optimal Metallic Salt-Ammonia Reaction Couple for Single Effect Solid-Gas Chemical Heat Pump

Jong Hun Han, Kil-Won Cho, Kun-Hong Lee† and Ho-Kyung Lee

Department of Chemical Engineering, Pohang University of Science and Technology,
San 31, Hyoja-Dong, Nam-Ku, Pohang 790-784, KyungBuk, South Korea
(*Received 1 November 1999 • accepted 10 December 1999*)

Abstract−A comparison of the coefficient of performance (COP), the specific cooling power (SCP) and the reactor volume per output power was carried out with numerous metallic salt-ammonia couples for single effect solid-gas chemical heat pumps. Optimal reaction couples could be selected in terms of COP, SCP and reactor volume at each application domain of deep freezing (−15~−20 °C), ice making (−10~−5 °C) and air conditioning (0-10 °C).

Key words: Refrigeration, Metallic Salt-ammonia, Chemical Heat Pump

INTRODUCTION

Air conditioning or refrigeration based on the sorption heat pump (SHP) technology has been investigated since this technology makes use of natural refrigerants as a working fluid, which does not affect the environment in term of ozone depletion and global warming [Pons et al., 1999]. Among the various SHP technologies, chemical heat pumps (CHPs) utilize the thermal effect of reversible chemical reactions involving a solid reactant and a gas. The solid-gas reactions of the following type have been widely used in the CHP technologies.

$$M\cdot(NH_3)_xCl_2 \Leftrightarrow M\cdot(NH_3)_yCl_2+\gamma NH_3 \tag{1}$$

Where M is the alkaline earth or transition metal and γ the change of stoichiometric coefficient (x-y). As the solid-gas equilibrium is monovariant, the thermodynamic cycle can be represented in the Clausius-Clapeyron diagram as shown in Fig. 1, where three temperature levels are required for the refrigeration process: T_l (low temperature), T_o (middle temperature) and T_h (high temperature).

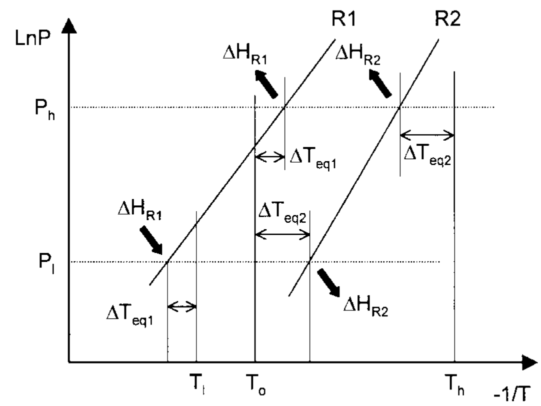

Fig. 1. Thermodynamic cycle for cold production in the Clausius-Clapeyron diagram.

Before any numerical analysis and construction of CHPs, a preliminary study to select the reaction couples should be performed in advance. Goetz et al. presented a method to select the optimal couple or process for given operating conditions in the single effect solid-gas CHPs using two criteria of COP and exergetic efficiency [Goetz et al., 1993]. Neveu et al. presented the relative performance of various solid-gas CHPs with internal heat recovery cycles depending on the reaction couples used and the power and temperature levels available [Neveu and Castaing, 1993]. However, they did not consider the cooling power per unit mass and the reactor volume per kW in selecting the optimal couples. Furthermore, their investigation was limited to a small number of metallic salts-ammonia couples. In this communication, the optimal couples are presented for the single effect CHP with four solid-gas reactors, which can be operated in pseudo continuous way, considering four important factors: the COP, the SCP, the reactor volume per kW of cooling load and the temperature of application.

THEORY

Fig. 1 shows the two main phases in the cycle for the cold production. In the low pressure (P_l) phase, cold heat is produced at low temperature (T_l), and in the high pressure (P_h) phase, desorption takes place at high temperature (T_h) from a heat source. Two intermediate stages are necessary to heat or cool reactors. The sensible heat in the form of thermal mass of the reaction bed, which cannot be recovered during the two main phases, is involved in the two non-productive stages. Thus, the theoretical COP can be given as follows.

$$COP_t=\frac{\gamma\Delta H_{R1}-C_{P,R1}^{loaded}(T_o-T_l)}{\gamma\Delta H_{R2}+C_{P,R2}^{loaded}(T_h-T_o)} \tag{2}$$

Where, ΔH_R and C_P^{loaded} are the enthalpy of reaction and the specific heat of metallic salt with fully ammoniated state, respectively.

At first, through the combination of 36 existing metallic salts [Neveu and Castaing, 1993], 125 reaction couples satisfying the

†To whom correspondence should be addressed.
E-mail: ce20047@postech.ac.kr

following conditions are selected and the COPs are then evaluated for the reaction couples.

– cold production temperature, T_l : –20-10 °C with the increment of 5 °C

– middle or heat sink temperature, T_o : 15 °C and 35 °C

– equilibrium temperature drop, $\Delta T_{eq1}/\Delta T_{eq2}$: 10/20 °C, 15/30 °C and 20/40 °C

– low operating pressure, P_l : 0.1-10.0 bar with the increment of 0.05 bar

From a practical point of view, for the reaction couples with similar COP_t, reactor volume per kW and SCP can be good criteria to select the optimal reaction couples. The graphite-metallic salt composite is investigated as a reaction bed in this work. The reactor volume and the mass of metallic salt can be then simply determined from the physical properties of the reaction bed such as bulk density, residual porosity and weight fraction of graphite. These calculations are carried out with the basis of the average output power and the cycle time of 1.0 kW and 1.0 hour in the stage of cold production.

The molar volume of ammoniated metallic salt can be well approximated by the following rule [Fujioka et al., 1996].

$$v_{salt}(n)=v_{salt}(0)+\beta\cdot n \tag{3}$$

Where v_{salt} is the molar volume of the metallic salt, n the moles of the NH_3 reacted with one mole of the metallic salt. β denotes the increase in molar volume per one mole of the NH_3 absorbed and is 19 cm^3/mol for ammoniates. With the benefit of molar volume data, calculation of the reactor volume and the SCP is possible as shown below.

The residual porosity, ϕ_r of the reaction bed can be expressed as follows.

$$\phi_r=1-\frac{\rho_b}{\rho_g}-\rho_b\left(\frac{1-w}{w}\right)\frac{v_{salt}^{loaded}}{M_{salt}} \tag{4}$$

Where, ρ_b is the bulk density defined as the mass of graphite divided by the total volume of the reaction bed, ρ_g the density of graphite (2,260 kg/m^3), w the weight fraction of graphite and M_{salt} the molar mass of salt. According to the previous work, ϕ_r and w were recommended to be over 0.3 and 0.15, respectively [Mazet et al., 1993]. In this work, ϕ_r and ρ_b are fixed as 0.6 and 200 kg/m^3, respectively. The mass of salt can be calculated as follows.

$$m_{salt}=\frac{P_r\cdot t_c\cdot M_{salt}}{\Delta H_r\cdot\gamma\cdot\Delta X} \tag{5}$$

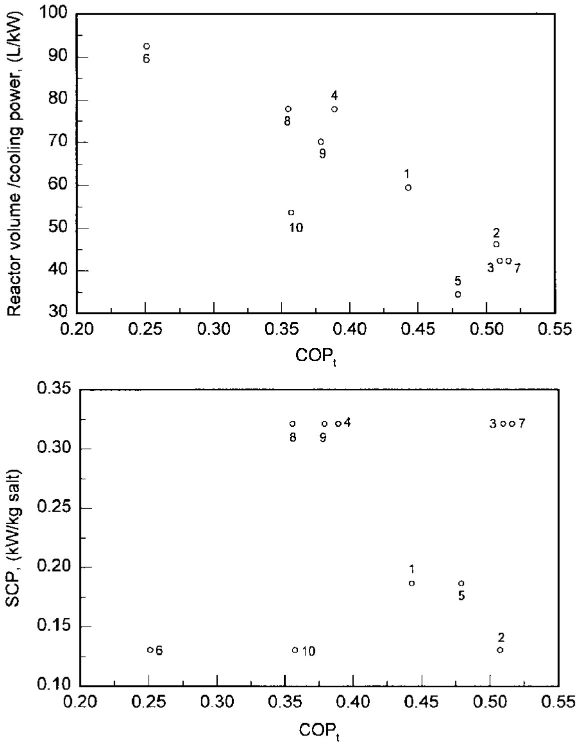

Fig. 2. Comparison of reaction couples in the application of ice making (T_o=15 °C).

1: Sn 9-4/Sn 4-2.5	6: Pb 8-3.25/Pb 2-1.5
2: Pb 8-3.25/Ca 4-2	7: Ba 8-0/Zn 6-4
3: Ba 8-0/Zn 6-4	8: Ba 8-0/Pb 2-1.5
4: Ba 8-0/Pb 2-1.5	9: Ba 8-0/Pb 1.5-1
5: Sn 9-4/Sr 8-1	10: Pb 8-3.25/Zn 6-4

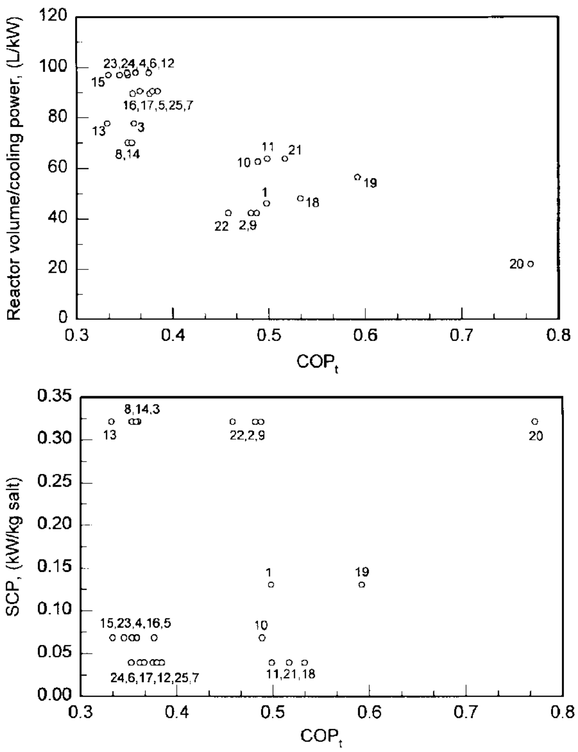

Fig. 3. Comparison of reaction couples in the application of air-conditioning (T_o=15 °C).

1: Pb 8-3.25/Ca 4-2	14: Ba 8-0/Pb 1.5-1
2: Ba 8-0/Zn 6-4	15: Sn 4-2.5/Pb 2-1.5
3: Ba 8-0/Pb 2-1.5	16: Sn 4-2.5/Pb 1.5-1
4: Sn 4-2.5/Pb 2-1.5	17: Pb 3.25-2/Pb 1.5-1
5: Sn 4-2.5/Pb 1.5-1	18: Pb 3.25-2/Mn 6-2
6: Pb 3.25-2/Pb 2-1.5	19: Pb 8-3.25/Pb 3.25-2
7: Pb 3.25-2/Pb 1.5-1	20: Ba 8-0/Sr 8-1
8: Ba 8-0/Pb 1.5-1	21: Pb 3.25-1/Zn 6-4
9: Ba 8-0/Zn 6-4	22: Ba 8-0/Zn 6-4
10: Sn 4-2.5/Zn 6-4	23: Sn 4-2.5/Pb 2-1.5
11: Pb 3.25-2/Zn 6-4	24: Pb 3.25-2/Pb 2-1.5
12: Pb 3.25-2/Pb 2-1.5	25: Pb 3.25-2/Pb 1.5-1
13: Ba 8-0/Pb 2-1.5	

Where P_r is the average output power, t_c the cycle time and ΔX conversion of reaction. The ΔX is given as 0.8 in this work. The weight fraction of graphite, w, can be calculated from Eq. (3) and then the volume of reaction bed, V_R is given as follows.

$$V_R=\frac{m_{salt}}{\rho_b}\frac{w}{1-w} \tag{6}$$

With the values of COP_t, the total volume of reactors per kW and the SCP were calculated as $(V_{R1}+V_{R2})$ per cooling power and cooling power per mass of metallic salt in R_1, respectively.

RESULTS AND DISCUSSION

According to the temperature of cold production, three typical applications [Pons et al., 1999] of the deep-freezing (−15~−20 °C), ice making (−10~−5 °C) and air conditioning (0-10 °C) were investigated in this work. Goetz et al. carried out the study of salt selection for Ba 8/0-Mn 6/2, Fe 6/2, Ca 4/2, Ca 8/4 and Zn 6/4 couples. The values of COP_t in this work are similar to those of COP_t calculated by Goetz et al. though a direct comparison is somewhat difficult because the thermodynamic equilibrium drop, ΔT_{eq}, is established in a different way.

For the deep freezing, low values of COP_t of 0.25-0.37 are evaluated for all the available couples. At T_o=15 °C, (R1) Pb 8(x)-3.25(y)/Zn 6-4 (R2) and Zn 10-6/Ca 8-4 couples show better COP_t compared to the other couples, while Pb 8-3.25/Mn 6-2 couples show a better COP_t at T_o=35 °C. Fig. 2 shows the comparison of available reaction couples in the application of ice making at T_o=15 °C. The values of COP_t are in the range of 0.25-0.52. In view of the small reactor volume, Sn 9-4/Sr 8-1, Ba 8-0/Zn 6-4 and Pb 8-3.25/Ca 4-2 couples can be selected as appropriate pairs. However, if we also consider the SCP and the COP, the Ba 8-0 /Zn 6-4 couple is evaluated as an optimal reaction pair at the conditions of T_l=−10 °C, T_h=104 °C and ΔT_{eq}=10/20 °C. Fig. 3 shows the comparison of available reaction couples in the application of air-conditioning at T_o=15 °C. The value of COP_t lies in the range of 0.33-0.77. By considering the reactor volume, the COP and the SCP, Ba 8-0/Sr 8-1 couple is evaluated as the optimal reaction pair with the conditions of T_l=10 °C, T_h=82 °C and

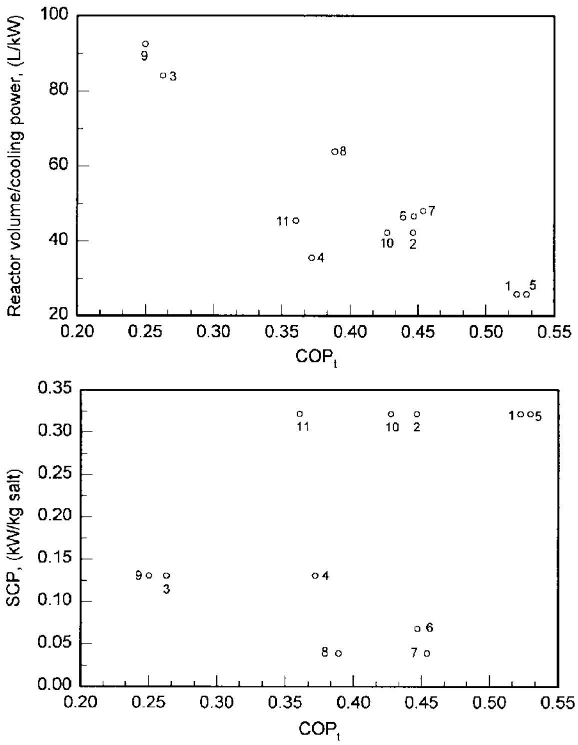

Fig. 4. Comparison of reaction couples in the application of ice making (T_o=35 °C).

1: Ba 8-0/Mn 6-2
2: Ba 8-0/Zn 4-2
3: Pb 8-3.25/Mn 6-2
4: Pb 8-3.25/Mn 6-2
5: Ba 8-0/Mn 6-2
6: Sn 4-2.5/Mn 6-2
7: Pb 3.25-2/Mn 6-2
8: Pb 3.25-Zn 4-2
9: Pb 8-3.25/Pb 2-1.5
10: Ba 8-0/Zn 4-2
11: Ba 8-0/Cu 5-3.3

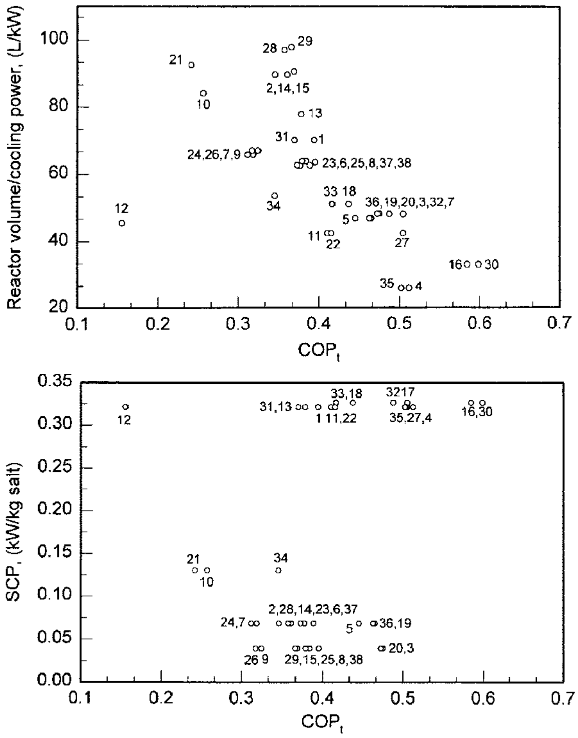

Fig. 5. Comparison of reaction couples in the application of air conditioning (T_o=35 °C).

1: Ba 8-0/Pb 1.5-1
2: Sn 4-2.5/Pb 1.5-1
3: Pb 3.25-2/Mn 6-2
4: Ba 8-0/Mn 6-2
5: Sn 4-2.5/Mn 6-2
6: Sn 4-2.5/Zn 4-2
7: Sn 4-2.5/Cu 5-3.3
8: Pb 3.25-2/Zn 4-2
9: Pb 3.25-2/Cu 5-3.3
10: Pb 8-3.25/Pb 1.5-1
11: Ba 8-0/Zn 4-2
12: Ba 8-0/Cu 5-3.3
13: Ba 8-0-2/Pb 2-1.5
14: Sn 4-2.5/Pb 1.5-1
15: Pb 3.25-2/Pb 1.5-1
16: Ca 8-4/Mn 6-2
17: Ca 8-4/Zn 4-2
18: Ca 8-4/Cu 5-3.3
19: Sn 4-2.5/Mn 6-2
20: Pb 3.25-2/Mn 6-2
21: Pb 8-3.25/Pb 2-1.5
22: Ba 8-0/Zn 4-2
23: Sn 4-2.5/Zn 4-2
24: Sn 4-2.5/Cu 5-3.3
25: Pb 3.25-2/Zn 4-1
26: Pb 3.25-2/Cu 5-3.3
27: Ba 8-0/Zn 6-4
28: Sn 4-2.5/Pb 2-1.5
29: Pb 3.25-2/Pb 2-1.5
30: Ca 8-4/Mn 6-2
31: Ba 8-0/Pb 1.5-1
32: Ca 8-4/Zn 4-2
33: Ca 8-4/Cu 5-3.3
34: Pb 8-3.25/Zn 6-4
35: Ba 8-0/Mn 6-2
36: Sn 4-2.5/Mn 6-2
37: Sn 4-2.5/Zn 4-2
38: Pb 3.25-2/Zn 4-2

ΔT_{eq}=10/20 °C. In case the cold production temperature is limited to 0 °C<T_l<5 °C, the Ba 8-0/Zn 6-4 couple becomes an appropriate reaction pair.

Fig. 4 shows the comparison of available reaction couples in the application of ice making at T_o=35 °C. The value of COP_t is in the range of 0.25-0.53. Again, by considering the reactor volume, the COP and the SCP, Ba 8-0/Mn 6-2 couple is evaluated as the optimal reaction pair with the conditions of T_l=5−10, −5 °C, T_h=157 °C and ΔT_{eq}=10/20 °C. Fig. 5 shows the comparison of available reaction couples in the application of air conditioning at T_o=35 °C. The value of COP is in the range of 0.16-0.60. In view of COP and SCP, the Ca 8-4/Mn 6-2 couple can be selected as an appropriate pair with the conditions of T_l=5, 10 °C, T_h= 133 °C and ΔT_{eq}=10/20 °C. In view of reactor volume and SCP, the Ba 8-0/Mn 6-2 couple can be selected as an appropriate pair with the conditions of T_l=0, 10 °C, T_h=179, 201 °C and ΔT_{eq}= 15/30, 20/40 °C. We should note that the exergetic efficiency becomes diminished as the temperature of the heat source, T_h, increases due to the larger heat loss from system to surroundings. Moreover, in some cases, the optimal reaction couples may be altered depending on available heat sources.

CONCLUSION

In this communication, the optimal metallic salt-ammonia couples for CHPs could be selected as a function of the application temperature and the heat source. In the application of a low temperature of −15~10 °C, the reactants can be used among the eight chlorides of Ba, Fe, Ca, Zn, Mn, Pb, Sn and Sr depending on the application domain. The improvement in the COP and SCP is possible by adapting internal heat recovery cycle using both the sensible heat and the heat of reaction. The CHP systems based on metallic salt-ammonia couples and useful heat sources such as industrial waste heat, solar energy and geothermal energy are expected to provide an alternative to vapor compression machines that use environmentally unfavorable CFCs or its derivatives as working fluids.

ACKNOWLEDGEMENT

Authors are pleased to acknowledge the financial assistance for research promotion project of the R&D Management Center for Energy and Resources (RaCER) to this work.

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