Characteristics of Water-Calcium Chloride and Water-Lithium Bromide Absorption Heat Pumps

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Introduction

An absorption heat pump, shown schematically in Figure 1, is a device for raising the temperature of low-grade heat energy to a more useful level using a relatively small amount of higher grade heat. The primary circuit consisting of an evaporator, a condenser, and an expansion valve is identical to that of a mechanical vapor-compression heat pump. However, a secondary or absorption circuit consisting of an absorber and a generator replaces the compressor used in a mechanical vapor-compression heat pump. The heat economizer shown in Figure 1 affects the efficiency but not the basic operation of the system.

A coefficient of performance (COP) for an absorption heat pump is normally defined as the ratio of the sum total of the heat delivered from the condenser and absorber ($Q_{CO} + Q_{AB}$) to the input of high grade heat energy Q_{GE}.

$$\mathrm{COP} = \frac{(Q_{CO} + Q_{AB})}{Q_{GE}} \tag{1}$$

Aqueous solutions of lithium bromide exhibit large negative deviations from Raoult's law that make them attractive for use in absorption heat pumps. Figures 2a and 2b are plots of salt concentration against generator temperature showing the effect of negative deviations from Raoult's law for the water-lithium bromide and the water-calcium chloride systems, respectively. The Raoult law lines in these figures are plotted and modified to give wt. % instead of mole fraction. A further advantage of a negative deviation from Raoult's law is to give a higher condenser temperature, T_{CO}, for a given generator temperature, T_{GE}, since a lower salt concentration is required.

Haseler (1980) calculated the theoretical maximum obtainable coefficient of performance COP_{AHMO} for an absorption heat pump from enthalpies H for various points in the cycle shown in Figure 1 and the flow ratio (FR) using Eqs. 2 and 3.

$$\mathrm{COP}_{AHMO} = \frac{H_4 - H_7 + \mathrm{FR}(H_7 - H_8) + H_1 - H_2}{\mathrm{FR}(H_5 - H_{10}) + H_1 - H_5} \tag{2}$$

$$\mathrm{FR} = \frac{M_{AB}}{M_W} \tag{3}$$

Alternatively the flow ratio, FR, can be calculated from the wt. % salt concentration in the generator, X_{GE}, and in the absorber, X_{AB}, using Eq. 4.

$$\mathrm{FR} = \frac{X_{GE}}{X_{GE} - X_{AB}} \tag{4}$$

In practice, actual coefficients COP_A are less than theoretical maximum obtainable coefficients of performance COP_{AHMO} calculated from Eq. 2 because of unavoidable thermodynamic inefficiencies.

The heat pump effectiveness (HPE) for an absorption heat pump, HPE_{AHMO}, is given by Eq. 5.

$$\mathrm{HPE}_{AHMO} = \frac{\mathrm{COP}_A}{\mathrm{COP}_{AHMO}} \tag{5}$$

Relative merits of calcium chloride and lithium bromide

Lithium bromide is thermodynamically the preferred salt for use in aqueous salt absorption heat pumps because of its relatively high solubility and the resulting large negative deviations from Raoult's law. An increase in temperature from 0° to 60°C increases the solubility of lithium bromide from 56.8 to 66.5

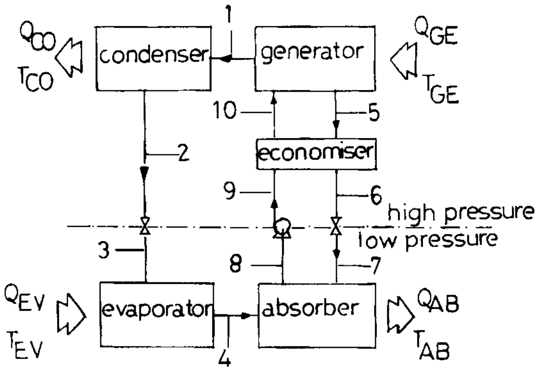

Figure 1. Block diagram of absorption heat pump.

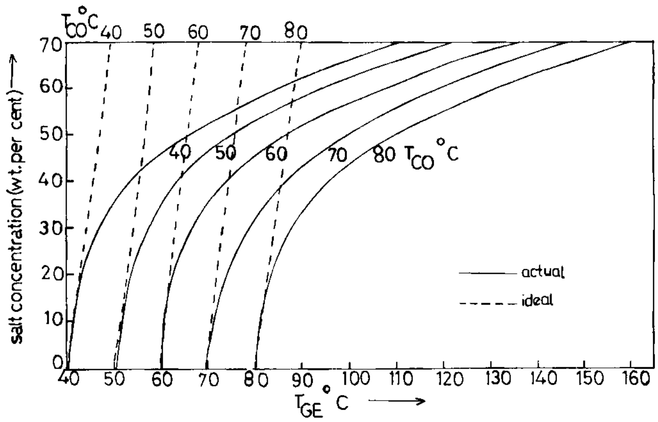

Figure 2b. Lithium bromide concentration vs. generator temperature.

wt. % and the solubility of calcium chloride from 37.3 to 57.8 wt. %. However, lithium bromide is more expensive and less readily obtainable than calcium chloride. Although calcium chloride is less soluble and produces slightly smaller negative deviations from Raoult's law than lithium bromide, aqueous calcium chloride solutions have the advantage of being significantly less corrosive than aqueous lithium bromide solutions.

A further incentive to reduce the use of lithium bromide arises from its potential medical hazards. Sax (1979) stated that inorganic bromides can produce depression, emaciation, and in severe cases, psychoses and mental deterioration. Bromide rashes (bromoderma), especially of the face, resembling acne and furanculosis, often occur when bromide inhalation is prolonged.

Theoretical performance analysis

Figure 3 is a plot of theoretical maximum obtainable coefficient of performance COP_{AHMO} (calculated from Eq. 2) against flow ratio FR, together with a plot of temperature T_{GE} and gross temperature lift $(T_{CO} - T_{EV})$ against FR for water-calcium chloride and water-lithium bromide systems, respectively, for a temperature $T_{CO} = T_{AB} = 70°C$. The calculations were done for generator salt concentrations X_{GE} in the range of 51.5 to 49.4 wt. % and flow ratios FR in the range 10 to 40. The pressures and temperatures at various state points in Figure 1 were calculated using the *P-T-X* data of McNeely (1979) for aqueous solutions of lithium bromide and *P-T-X* data of Siddig-Mohammed et al. (1983) for aqueous solutions of calcium chloride. The solution enthalpies were calculated for each of these conditions by interpolating the *H-T-X* data of McNeely for water-lithium bromide and the *H-T-X* data of Siddig-Mohammed et al. for water-calcium chloride. The enthalpies of water were taken from the tables of Keenan et al. (1969). The efficiency of the economizer heat exchanger was 0.7.

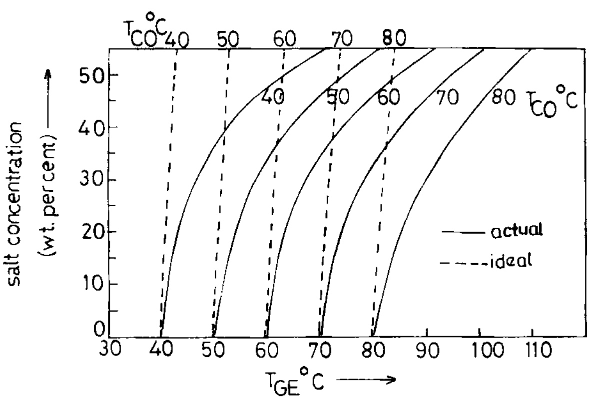

Figure 2a. Calcium chloride concentration vs. generator temperature.

Figure 3 shows that for both systems COP_{AHMO} and T_{GE} values decrease and $(T_{CO} - T_{EV})$ values increase with increasing flow ratios FR. For a given salt concentration, the values of $(T_{CO} - T_{EV})$ and COP_{AHMO} differ only marginally for the two systems.

Experimental

The experiments were carried out in a glass absorption heat pump shown schematically in Figure 4. This consisted, for the most part, of standard items supplied by Quickfit Ltd., U.K.

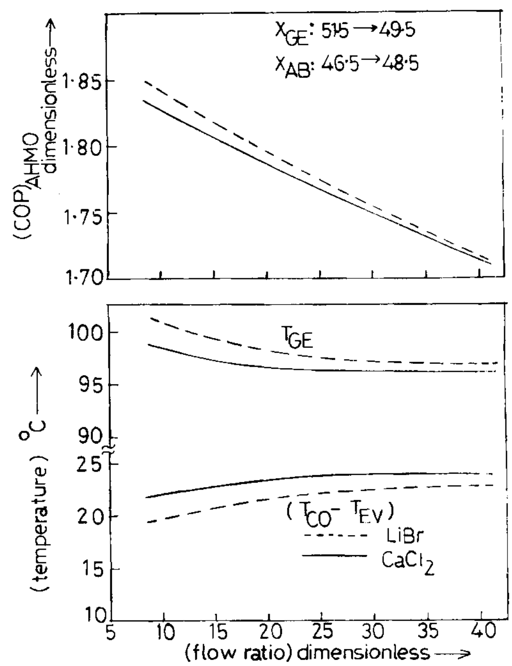

Figure 3. Temperature and theoretical maximum obtainable coefficients of performance vs. flow ratio.

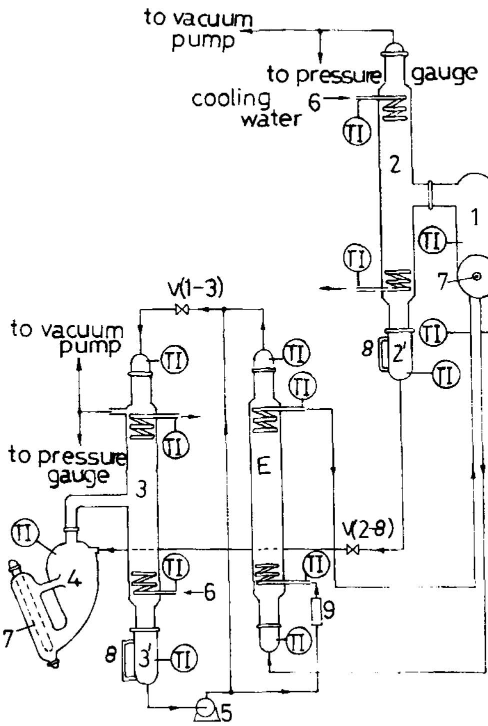

Figure 4. Diagram of experimental absorption heat pump.

1. generator
2. condenser
3. absorber
4. evaporator
5. solution pump
6. cooling water
7. heater
8. sight glass
9. rotameter

E, economizer
V, expansion valve

The experimentally determined relationship between the salt concentration X in wt. % and the refractive index n_D was:

1. $X = -511.95 + 505.895\ n_D - 79.8105\ n_D^2$ for aqueous lithium bromide solutions (at 35°C), with a maximum error of 0.234%.

2. $X = -864.751 + 893.173\ n_D - 182.492\ n_D^2$ for aqueous calcium chloride solutions (at 40°C), with a maximum error of 0.278%.

3. $X = -396.982 + 267.717\ n_D + 27.7525\ n_D^2$ for 1:1 aqueous calcium chloride/lithium bromide solutions (at 40°C), with a maximum error of 0.583%.

The 1:1 solution mixture of $CaCl_2$ and LiBr was chosen because it was expected that this ratio would give a lower risk of crystallization without any other undesirable properties.

In order to achieve a steady state, it was necessary for the mass flow rate of water leaving the generator to equal that entering the absorber so that

$$M_{AB} = M_{GE} + (M_W)_{EV} \tag{6}$$

and

$$(M_W)_{CO} = (M_W)_{EV} \tag{7}$$

Equations 6 and 7 imply that at a steady state the liquid levels in the generator, absorber, and evaporator remained constant. This was achieved by balancing the heat loads Q_{GE} and Q_{EV} and the cooling water rates to the condenser and the absorber for each flow ratio FR. The temperature of the condenser and absorber was maintained at about 70°C and the flow ratios were varied between 10 and 40. The readings were taken after reaching steady state.

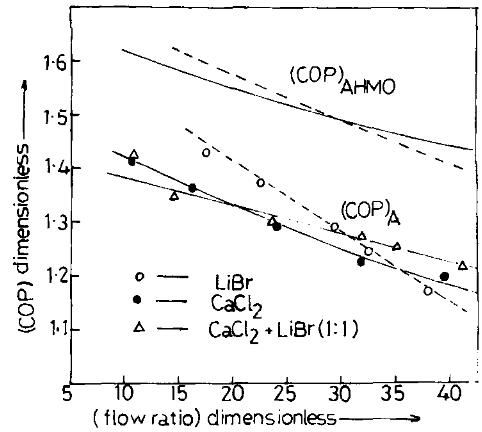

Figure 5. Coefficients of performance vs. flow ratio.

Results and Discussion

The experimentally determined data are plotted in Figures 5, 6, and 7. Figure 5 is a plot of actual coefficient of performance COP_A and theoretical maximum obtainable coefficient of performance COP_{AHMO} against flow ratio FR for three aqueous salt systems: calcium chloride, lithium bromide, and a 1:1 mixture of calcium chloride and lithium bromide. Both COP_A and COP_{AHMO} decreased with an increase in FR.

Figure 6 is a plot of generator temperature T_{GE} and gross temperature lift $(T_{CO} - T_{EV})$ against flow ratio FR for the three systems. Kumar et al (1984) previously observed that T_{GE} decreased with an increase in FR, and the data plotted in Figure 6 confirm this. This decrease in T_{GE} is due to a decrease in the salt concentration in the generator X_{GE}. Figures 5 and 6 illustrate that absorption heat pumps operating on aqueous salt systems should be operated at relatively low flow ratios in order to avoid a significant decrease in the actual coefficient of performance COP. The gross temperature lift $(T_{CO} - T_{EV})$ is relatively independent of FR. Figures 5 and 6 also show that the experimental results for the variation of COP_A, T_{GE}, and

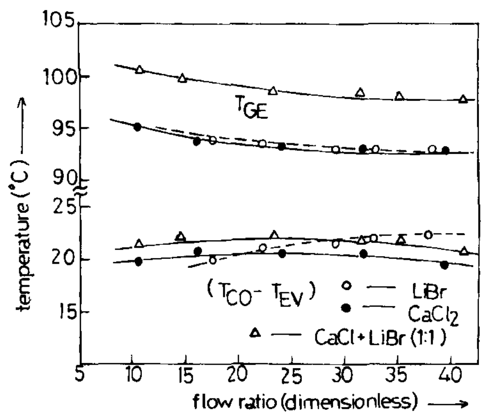

Figure 6. Temperature vs. flow ratio.

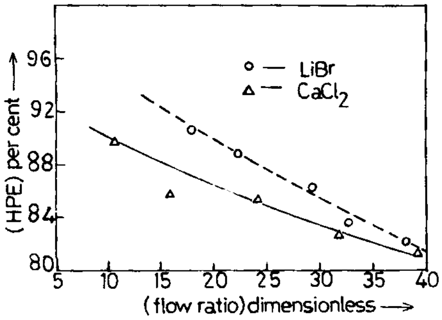

Figure 7. Heat pump effectiveness vs. flow ratio.

$(T_{CO} - T_{EV})$ with FR are consistent with the theoretical plots in Figure 3.

The ranges of experimental values of COP_A obtained for the three aqueous salt systems were:

1. 1.42 to 1.17 for lithium bromide with X_{GE} = 48 to 47.1 wt. % and $(T_{CO} - T_{EV}) \simeq 20°C$.
2. 1.41 to 1.19 for calcium chloride with X_{GE} = 49.4 to 47.6 wt. % and $(T_{CO} - T_{EV}) \simeq 20°C$.
3. 1.42 to 1.17 for a 1:1 mixture of calcium chloride and lithium bromide with X_{GE} = 51.5 to 49.2 wt. % and $(T_{CO} - T_{FV}) \simeq 21.5°C$.

Figure 7 is a plot of heat pump effectiveness HPE_{AHMO} calculated from Eq. 5 against flow ratio FR for aqueous solutions of calcium chloride and lithium bromide. HPE_{AHMO} decreased with an increase in FR for both systems with the rate of decrease for the H_2O-$CaCl_2$ system less than for the H_2O-LiBr system. HPE_{AHMO} values between 80 and 90% were obtained for both systems.

Conclusions

This experimental study has shown that a water-calcium chloride absorption heat pump can operate with coefficients of performance of between 80 to 90% of the theoretical maximum possible values. The values of the actual coefficient of performance were in the range 1.2 to 1.4. The operating performance is only marginally less than for a water-lithium bromide absorption heat pump within the solubility limits of calcium chloride. The risk of crystallization can be reduced by the addition of lithium bromide to calcium chloride. This enables higher salt concentrations to be used, which is necessary when higher gross temperature lifts are required.

Notation

COP = coefficient of performance
FR = flow ratio
H = enthalpy per unit mass, $kJ \cdot kg^{-1}$
HPE = heat pump effectiveness
M = mass flow rate, $kg \cdot s^{-1}$
n_D = refractive index
P = pressure, bar
Q = heat rate, kW
T = temperature, °C or K
x = mole fraction
X = weight fraction

Subscripts

A = actual
AB = absorber
$AHMO$ = theoretical maximum obtainable
CO = condenser
EV = evaporator
GE = generator
S = solution
W = water

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