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Heat and Mass Transfer Considerations in Advanced Heat Pump Systems*

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ABSTRACT

Advanced heat-pump cycles are being investigated for various applications. However, the working media and associated thermal design aspects require new concepts for maintaining high thermal effectiveness and phase equilibrium for achieving maximum possible thermodynamic advantages. In the present study, the heat- and mass-transfer processes in two heat-pump systems -- those based on absorption processes, and those using refrigerant mixtures -- are analyzed. The major technical barriers for achieving the ideal performance predicted by thermodynamic analysis are identified. The analysis provides general guidelines for the development of heat- and mass-transfer equipment for advanced heat-pump systems.

INTRODUCTION

Advanced heat-pump cycles are being investigated for various applications. They include absorption, chemical adsorption, thermomagnetic, direct conversion, thermoacoustic, and mixture (nonazeotropic) refrigerant heat pumps. They offer thermodynamic and other system integration related advantages over conventional mechanical vapor recompression (MVR) heat pumps. Many of the reported investigations have focused their studies on thermodynamic analysis of these heat-pump cycles while neglecting or minimizing heat- and mass-transfer resistances. However, the heat- and mass-transfer processes in these heat pumps could limit their thermodynamic advantages.

The single-effect absorption heat-pump cycle without any heat recovery device may not have a coefficient of performance (COP) comparable with that for MVR systems. Therefore, several absorption cycle analyses have been carried out to determine an approach for integrating the system and, hence, to improve the overall COP and to expand the temperature lift. The thermodynamic analysis reported by Phillips (1990) showed many variations of the basic cycle by employing various internal heat recovery schemes for gas-fired absorption heat pumps. The study showed that a substantial gain in COP can be achieved by implementing various internal

heat recovering systems, including the generator absorber heat exchanger (GAX). Similarly, the thermodynamic analysis of DeVault (1990) showed advantages for triple-effect ammonia/water heat pumps. Erickson (1991) developed a modified concept (Branched GAX) for further COP improvement for the GAX cycle.

In order to take thermodynamic advantage of nonisothermal heat sources and sinks, nonazeotropic refrigerant mixtures (NARMs) are being evaluated for MVR heat pumps. However, the heat- and mass-transfer resistances in such heat-pump systems reduce the overall performance significantly. Webb and DiGiovanni (1989) carried out an analysis; however, the heat-transfer calculation was simplified by assuming the log-mean temperature difference (LMTD) and by not taking account of the mass-transfer resistance. Their results indicated that no significant COP gain can be achieved by refrigerant mixtures. Examination of the results from the previous investigations (e.g., Haselden 1987; Mitsuda et al. 1990) shows that the mass-transfer resistance cannot be ignored; therefore, it is essential to evaluate appropriate heat- and mass-transfer enhancement techniques to minimize the effect of the resistance.

ABSORPTION HEAT PUMP CYCLE

Complexity of the heat- and mass-transfer processes in absorption heat pumps increases with integration to recover the internal heat energy. In order to minimize the thermodynamic irreversibility of the process, the mean temperature differences are maintained at relatively low values. As a result, the heat- and mass-transfer component has to operate at an optimum performance in a narrow range of conditions. Little work has been carried out to develop a heat- and mass-transfer component for advanced absorption heat pumps. Machielsen (1990) provided an overview of research work on absorption heat pumps and showed superior performance for two compact heat exchanger configurations as compared with commercial units. Ferreira et al. (1984) carried out an experimental program to determine the rate of absorption of ammonia in a vertical tube operated as a bubble column. The results were presented in terms of the Sherwood number, and the effects of operating parameters (e.g., liquid flow rate, heat flux, temperature, pressure, and tube diameter) were empirically correlated. The experimental results of Nakao et al. (1987) demonstrated that, by adding fins (commonly used

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for gas-phase heat transfer) to the tube, the rate of absorption of water vapor in an LiBr solution was enhanced by a factor of two. In the experimental investigation of Zaltash et al. (1991), the LMTD approach was used to analyze the rate of absorption of water in LiBr and (Li,K,Na)NO₃ solutions.

Recently, Brauner (1991) carried out an analysis for a laminar falling film to determine the rate of absorption of water in brine solutions. The analytical results showed that it is essential to formulate the analytical method by using the high-mass-flux transport equations.

It was stated by Ferreira et al. (1984) that the absorption of refrigerant, in general, limits the overall performance of heat pumps. Therefore, in the present study, the effects of heat and mass transfer on absorption are analyzed to determine the nonequilibrium conditions that may prevail in the absorber. In order to examine a specific case, a typical set of operating conditions reported by Herold et al. (1991) and Phillips (1990) for the GAX cycle is used in the present study; however, approximations are applied for some conditions for the sake of simplifying the equilibrium data.

OVERALL ABSORPTION PROCESS - The GAX heat-pump cycle is schematically presented in Fig. 1 (Phillips 1990). After transferring the sensible heat to the incoming mixture in the desorber (generator), the dilute mixture at point F enters the absorber along with refrigerant. The vapor and liquid mixtures, if they reach equilibrium, correspond to point M in the isobaric Ponchon diagram of Fig. 2, with corresponding vapor and liquid compositions represented by points V₁ and L₁, respectively. If the two phases remain in equilibrium at all times, absorption follows path MC in Fig. 2. Depending upon the cooling media temperature, the exiting mixture could reach a subcooled state below point C.

Figure 1. Pressure-Temperature Diagram for the GAX Cycle

Figure 2. Isobaric Ponchon Diagram for Ammonia/Water

It should be noted that the absorption process for the GAX cycle shown by path FC (Fig. 1) is divided into two operations. During the absorption path FM (GAX heat exchanger), the heat of absorption is used for the desorption of refrigerant in path DN. The remaining absorption takes place by rejecting heat to the strong solution (path CD) and cooling media (air or water). If split refrigerant flow is used for the above two operations, the equilibrium point for the GAX heat exchanger is represented by point F' in Fig. 2 with equilibrium points for vapor and liquid phases V₂ and L₂, respectively.

For other heat-pump systems (single and multi-effect), the absorption path is generally divided into more than one operation, which requires a careful integration of the absorber with the rest of the system.

HEAT AND MASS TRANSFER IN ABSORPTION - The local heat- and mass-transfer processes are illustrated by concentration profiles shown in Fig. 3. As absorption takes place, the interfacial temperature is expected to be greater than the bulk temperature. The refrigerant concentration in the liquid phase is higher at the interface than in the bulk, giving a corresponding concentration gradient in the vapor phase. The absorption heat released at the interface is diffused through the liquid film, conducted through the wall, and convected into the cooling media. As discussed in a previous study (Panchal and Arman 1991) and following the Colburn-Drew (1937) analysis, the mass-transfer rate for the vapor phase is expressed as follows:

$$N_T = N_1 + N_2 = K_g \ln \left[\frac{Z_1 - Y_{1b}}{Z_1 - Y_{1i}} \right] \quad (1)$$

$$\text{where:} \quad Z_1 = N_1 / N_T \quad (2)$$

Figure 3. Concentration and Temperature Profiles for the Absorption Process

The liquid-phase mass-transfer rate should be expressed in terms of refrigerant (component 1) as follows:

$$N_1 = k_l (x_{1b} - x_{1i}) + N_c x_{1i} \quad (3)$$

In addition to the continuity for the mass flux, the following heat-flux equation needs to be satisfied at the interface:

$$U_o (T_i - T_w) = h_g \frac{\Phi_T}{1 - \exp(-\Phi_T)} (T_v - T_i) + N_T (H_{vb} - h_{li}) \quad (4)$$

$$\text{where: } \Phi_T = N_T (Z_1 C_{p1} + Z_2 C_{p2}) \quad (5)$$

In the limiting case of negligible mass-transfer resistance, the calculation procedure can follow the design approach used for condensers as discussed by Bogart (1981). In such a design approach, the saturation curve (condensation or absorption) and the cooling-medium temperature are plotted against the heat duty. The effective mean temperature difference is then calculated by either numerically integrating or by using the inlet and outlet conditions. The heat-transfer area is calculated by using an empirical correlation for the effective (including the mass-transfer resistance) heat-transfer coefficient derived from the experimental data. An unknown level of design uncertainty arises if the experimental conditions, including geometric configuration of the test section, do not represent the prototype absorber.

In most cases, the mass-transfer resistance cannot be totally ignored; therefore, the set of equations shown above should be used for calculating the local rate of absorption. The equations for the local rate of heat- and mass-flux can be combined with the overall heat- and mass-balance equations to determine the overall performance of the absorber. Note that it requires a computerized design approach with a validated calculation method. However, it reduces the uncertainty for extrapolating the experimental data obtained from laboratory-scale apparatus to the prototype absorber.

EFFECTS OF ABSORBER CONFIGURATION - If the vapor and liquid phases were premixed to achieve the equilibrium point M in Fig. 2, it would avoid evaporation of water in the inlet region. For the cocurrent flow configuration, absorption could follow path MC in Fig. 2 in the absence of significant mass-transfer resistances. However, for the shell-side flow, the vapor and liquid flow paths cannot be clearly defined; therefore, a spatial distribution of local vapor- and liquid-phase concentration

would be produced. Such a distribution, in general, would reduce the overall thermal performance of the absorber. In an ideal cross-flow absorber where vapor and liquid phases flow down the shell-side and the coolant flows in a single-pass configuration, the rate of absorption will not be uniform along the tube length. At the cold inlet end, the solution would reach saturation conditions quickly, and part of the heat-exchanger surface would be ineffective for heat transfer. On the other hand, a pinch point might occur at the warm outlet end, which would also make part of the heat-transfer area ineffective. As a result, the thermal maldistribution created by the axial temperature gradient lowers the performance of the absorber. A multi-flow pass configuration might correct the thermal maldistribution problem to some extent, if the phases were well-mixed at each cross-section.

If the vapor and liquid phases are not mixed, evaporation of water and absorption of ammonia will take place near the entrance region. The relative paths for the two phases could have a significant effect on the local heat- and mass-transfer rates. The spatial distribution of the local concentration of the ammonia/liquid mixture should be calculated by integrating heat- and mass- balance equations.

The effects of cocurrent vs. countercurrent flow configurations on the local rate of heat and mass transfer can be evaluated by analyzing bulk conditions at the top and bottom points of the absorber. In the case of cocurrent flow at the top of the absorber, the liquid temperature is about 99 °C if the two phases are properly mixed to reach saturation conditions. Due to the mass-transfer resistance, the liquid-phase temperature would have to be lowered by the cooling medium before the absorption process could start. On the other hand, if the two phases were not premixed, the liquid and vapor temperatures would be about 145°C and 29°C, respectively. There would be simultaneous absorption of refrigerant and evaporation of water at the interface. The net enthalpy required at the interface would be provided by the sensible heat from the liquid phase as it is being cooled by the cooling medium. In the case of countercurrent flow, the vapor phase would have reached close to equilibrium with the liquid phase; therefore, evaporation of water would not take place, resulting in a higher heat flux at the top than that for the cocurrent flow configuration.

If the mass-transfer resistance is not significant, the rate of heat transfer would be determined by the bulk saturation temperature and the cooling medium temperature at the bottom of the absorber for the cocurrent flow configuration. Under such conditions, the absorption and cooling medium temperatures would follow path MC shown in Fig. 2. However, for the countercurrent flow configuration, the temperature path for the absorption process would not follow the same path. Under equilibrium conditions, the saturation temperature would be below point C in Fig. 2 at the bottom of the absorber. As a result, the local heat flux would be lower than that for the cocurrent flow configuration.

The discussion above is based on an assumption of negligible mass-transfer resistance. In the case of finite mass-transfer resistance, the local heat and mass fluxes would be significantly affected by the local values of heat- and mass-transfer coefficients.

DESORPTION PROCESS - The desorption (also called separation or generation) process can be compared with boiling a mixture of fluids that have a large difference in their boiling points. For the LiBr/water or (Li,Br,K)NO₃/water system, the vapor pressure of the salt is negligible; therefore, the desorption process is basically

nucleate boiling or thin-film evaporation of an aqueous solution. In general, the ammonia/water separation can be achieved in tray or packed-column distillation columns as discussed by Bogart (1981). However, for an energy-efficient separation and for heat sources where a limited temperature-driving force is available, the desorber should be designed for a continuous heat supply system along the equilibrium curve. However, as discussed later in the refrigerant mixture section, the effects of the mass-transfer resistance on nucleate boiling are significant due to a large difference in the vapor pressure of ammonia and water at a given temperature. The mass-transfer problem could be even worse for the LiBr/water system, where local build-up of salt concentration could cause undesired precipitation. The heat- and mass-transfer processes for thin-film desorption are similar to those for absorption; however, the liquid-side and the vapor-side mass-transfer resistances are expected to be the controlling mechanisms. The rate-governing equations discussed for absorption are applicable for desorption.

HEAT AND MASS TRANSFER IN GAX HEAT EXCHANGER - The heat- and mass-transfer processes in the GAX heat exchanger are further complicated by the requirement that absorption and desorption of refrigerant take place in a single unit in a countercurrent flow configuration. A typical set of operating conditions (Phillips 1990; Herold 1991) are shown schematically in Fig. 4. The GAX heat exchanger needs to be integrated with the absorber where heat is rejected to the ammonia/water solution and to the cooling medium (air or water). In the branched-GAX system (Herold et al. 1991), the rate of heat transfer for absorption is balanced with that for desorption by splitting the flow stream. In a normal set of design conditions, the liquid phase would be distributed at the top with cocurrent or countercurrent vapor flow for the absorber. For desorption, the liquid-phase would be introduced at the bottom, and the two-phase flow mixture would exit from the top. As discussed in the previous section, the saturation temperature profile for absorption and desorption should be plotted along the length of the heat exchanger for both the cocurrent and countercurrent configurations for the absorber. Such a design approach should help to identify the possibility of a pinch point under conditions of finite mass-transfer resistance.

REFRIGERANT MIXTURES

The local rate of heat and mass transfer for binary refrigerant mixtures can be represented by Fig. 3 following the Colburn-Drew (1937) analysis. Haselden (1987) discussed the heat- and mass-transfer issues for refrigerant mixtures. The effects of liquid-side mass-transfer coefficient on the rate of condensation was analyzed by examining the limiting cases of perfectly mixed and no mixing of the liquid phase. It was shown that the cooling medium would have to be below the boiling point of the lower boiling fluid for the case of no mixing. The no mixing case would arise for the very low liquid-side mass-transfer coefficient or for the heat exchanger configuration where the condensate liquid is detached from the heat-transfer surface (e.g., horizontal shell-side condensation). Kornota and Stoecker (1985) studied flow regimes for refrigerant mixtures condensing inside horizontal tubes. Mitsuda et al. (1990) and Shotani (1990) obtained binary condensation data for a compact heat exchanger. They noted that the effective heat-transfer coefficient for binary mixtures was significantly lower than that for pure components.

Figure 4. Schematic Diagram Showing Operating Conditions for the GAX Absorber

The mass-transfer resistance has similar effects on evaporation of refrigerant mixtures. The experimental results reported by Jung and Didion (1989) show that the effective (including the mass-transfer resistance) heat-transfer coefficient is lower than that for individual components under similar operating conditions (e.g., mass quality and heat flux). Thome (1990) and Collier (1981) provided a detailed summary of the literature data to characterize the effects of mass transfer on nucleate boiling. In general, the mass-transfer resistance during the transient heat transfer of bubble growth in nucleate boiling reduces the effective heat-transfer coefficient as compared with that for individual components. The resulting effect in the flow boiling case could be lengthening of the region where nucleate boiling is a dominating mode of heat transfer. Lengthening of this region, which includes bubble and slug flows, reduces the overall heat-transfer coefficient because the combined (nucleate plus convective) heat-transfer coefficient is lower in this region than that for the fully developed annular flow region where the convective heat-transfer coefficient is significantly high; however, in the annular flow regime, the mass-transfer resistance in the liquid film may be critical. Various semi-empirical correlations have been tried to correlate the experimental data for nucleate and forced-convective boiling of mixtures; however, a validated design method that can take into account the effects of mass transfer is lacking.

EFFECTS OF PHASE SEPARATION -

Phase separation is an important design criterion for selecting the heat- and mass-transfer component for refrigerant mixtures. If the two phases do not flow in intimate contact, then the local equilibrium condition and corresponding saturation temperature cannot be easily calculated. For example, consider the vapor/liquid diagram shown in Fig. 5 for the R22/R114 mixture studied by Jung and Didion (1989). In the case of condensation of this mixture in a horizontal tube, a typical flow regime (shown in Fig. 6) can occur under a wide range of flow conditions. The bulk of vapor and liquid phases will not be in local equilibrium. Condensate liquid formed in the thin-

film region of CAB flows down to mix with the bulk of liquid flowing axially. Equilibrium conditions exist only at the vapor-liquid interfaces of the thin-film and bulk-flow regions. The bulk of liquid flowing in the bottom of the tube may be perfectly mixed, but the liquid formed in the thin-film region has a different composition than that for the bulk of liquid. As a result, the condensation process for the thin-film region follows a different condensation curve than that determined by assuming bulk equilibrium conditions. The condensation process for the thin-film region closely follows the no mixing case. The equilibrium liquid-phase composition in this region is determined by the continuity of the mass flux at the interface as shown below:

$$X_{1i} = N_1/N_T \quad X_{2i} = N_2/N_T \quad (6)$$

Figure 5. Temperature-Composition Diagram for R114/R22 Mixture

Figure 6. Two-Phase Flow Schematic for the Convective Condensation/Boiling in Horizontal Tube

The condensation curve follows the dew point line in Fig. 5, and no further condensation can take place below the dew point, D_1 , which corresponds to the coolant temperature, C_1 . In a real application, the condensation pressure increases until the boiling point of the pure component, D_0 , is greater than the coolant temperature, which in effect lowers the COP value and diminishes the thermodynamic advantages of the refrigerant mixture. Note that the single-component heat-

transfer coefficient is relatively high for the thin-film region; however, the phase separation and mass-transfer resistance limit the rate of condensation. On the other hand, the single-component heat-transfer coefficient for the bottom part is relatively low. The combined effect reduces the effective heat flux as compared with that predicted by assuming equilibrium conditions.

A similar conclusion can be drawn for forced-convective evaporation in a horizontal tube: a concentration gradient is expected along the periphery of the tube surface. At low vapor velocities, the thin-film region could be dry or the liquid phase would have a high concentration of the less volatile component, which would raise the interfacial temperature higher than that for the lower part of the tube where the bulk of liquid flows. It would reduce the heat flux in this region, although the single-component heat-transfer coefficient is relatively high due to the thin liquid film. In their experimental study, Jung and Didion (1989) observed a significant temperature difference between the top and bottom parts of the tube for the refrigerant mixtures compared with that for pure components. The temperature difference for the refrigerant mixtures was up to 4°C for mass qualities in the range of 20-60% as compared with about 0.1-0.3°C for pure components. However, the two wall temperatures were relatively close for high mass qualities (>60%). Note that the liquid phase is more uniformly distributed for high mass qualities, resulting in a less severe gradient of the local saturation temperature. Measurements indicated a peripheral concentration gradient along the tube surface. As expected, the heat-transfer coefficient for the top part was higher than for the bottom part for pure components. However, the effective heat-transfer coefficient for the top part was lower than that for the bottom part for refrigerant mixtures. These observed results clearly show the effects of the mass-transfer resistance and phase separation on the local rate of heat and mass transfer.

ADVANCED HEAT- AND MASS-TRANSFER COMPONENT

The non-equilibrium -- global as well as local -- conditions between the liquid and vapor phases significantly reduce the COP value for heat pumps as compared with those predicted from the thermodynamic analysis. Therefore, the following two design criteria should be adopted to overcome factors affecting the overall rate of heat- and mass-transfer:

- Maintain intimate contact between the liquid and vapor phases, and
- Develop enhancement techniques for the mass-transfer resistance.

In order to keep the two phases together, the heat and mass transfer of the mixture should be carried out in vertical flow channels where possible and sufficient vapor velocities should be maintained in all cases. For horizontal flow configurations, narrow channels should be considered, with some device to mix the liquid and vapor phases periodically to offset the concentration gradient buildup. The possibility of maldistribution caused by the inlet and outlet headers should be avoided.

In the past, the development of heat-transfer enhancement techniques has focused on increasing heat transfer across the liquid film or promoting nucleate boiling. However, little work has been done for the development of enhancement techniques for simultaneous heat- and mass-transfer process applications. Such enhancement techniques should have the following characteristics:

- Continuous contact between the liquid and vapor phases;
- A liquid phase that remains on the wall to transfer or gain heat from the wall surface;
- Swirling flow mechanisms for the liquid phase to enhance the liquid-phase heat- and mass-transfer coefficient;
- An extended surface to provide additional mass-transfer area, even though the extended surface may not transfer heat efficiently; and
- Suitable flow channels to increase the vapor-phase mass-transfer coefficient.

CONCLUSION

The analysis shows that the mass-transfer resistance and possible phase separation could limit the thermodynamic advantages of absorption and refrigerant-mixture heat pumps. The use of commercial heat- and mass-transfer components and present design tools are not adequate for the new configurations and enhancement techniques developed for advanced heat-pump systems.

NOMENCLATURE

C_p	Specific heat	J/mol K
H_v	Vapor-phase enthalpy	J/mol
h_l	Liquid-phase enthalpy	J/mol
h_g	Vapor-phase liquid-side heat-transfer coefficient	W/m ² K
K_g	Vapor-phase mass-transfer coefficient	mol/s m ²
k_l	Liquid-phase mass-transfer coefficient	mol/s m ²
N	Mass flux	mol/s m ²
T	Temperature	°C
U_o	Liquid-phase heat-transfer coefficient	W/m ² K
X	Liquid-phase mole fraction	
Y	Vapor-phase mole fraction	
Z	Fractional mass flux	

Subscript

$1,2$	Component 1 or 2
i	Interface
b	Bulk
c	Convective term of diffusion
w	Wall
T	Total

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