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Limits of mass transfer enhancement in lithium bromide–water absorbers by active techniques

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Abstract—A model to predict the theoretical limits of mass transfer enhancement in a falling film absorber using LiBr aqueous solution has been developed and it provides a means of comparative absorber performance evaluation. During vapor absorption, the vapor–liquid interface becomes saturated immediately after it is exposed to vapor. Further absorption can only be sustained by mass diffusion and heat conduction into the fluid bulk, assuming a stationary interface. Due to the relatively small heat and mass diffusivities of LiBr aqueous solution, the mass absorption rates sustained by pure diffusion and conduction processes are small. To increase the mass absorption rates, mixing of the solution is favored. Therefore, every mass transfer enhancement technique, passive or active, consists of basically disturbing the film and causing mixing of the solution near the interface. The higher the mixing rate, the higher the mass absorption rate. To assess the effect of a mixed interface, a mathematical model is formulated. This model solves one-dimensional heat and mass differential equations coupled at the interface. An asymptote of the mass transfer rate as the mixing rate increases is derived. The model, which takes into account all relevant parameters such as temperatures, pressures, concentrations, mass flow rates, and geometry, is an ideal tool for rating absorber performance. Results show that, under typical operating conditions found in commercial chillers, the theoretically possible maximum mass absorption rate is 0.049 kg $m^2 \cdot s^{-1}$, and that, at a mechanically feasible mixing frequency of 1000 Hz, a mass absorption rate of 0.0256 kg $m^2 \cdot s^{-1}$ is possible. The latter rate is about an order of magnitude larger than that found in commercial chillers. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Absorption chillers containing no chlorofluorocarbons are considered environmentally friendly and are a competitive alternative to conventional vapor compression chillers. The most commonly used working pair for absorption chillers is LiBr/water. However, problems inherent in using LiBr/water have long made designing efficient, compact chillers a real challenge. The absorption rates are a direct measurement of machine capacity. However, the rates are strongly affected by a large number of variables. The designer must then control the variables in question to obtain an acceptable design. Among the variables affecting absorber performance, one can identify the following: (1) non condensables. As the absorbers operate under vacuum, and also corrosion and passivation take place, non condensable gases, which hinder absorption, are generated. These gases must be removed for proper operation. (2) Solution distribution. The solution is usually sprayed over the absorber tubes. However, complex surface phenomena and flow instabilities conspire against a uniform film flowing downwards over the absorber tubes. For a given Reynolds number, the flow instabilities are more pronounced the smaller the tube to tube spacing. The flow regimes obtained in most absorbers defy complete analytical treatment. (3) Thermal and molecular diffusions. During absorption, it is necessary to remove the heat of absorption and to transfer absorbate from the interface into the bulk. The rate of mass transport is primarily governed by the diffusion coefficient, which is not large for water–salt solutions, and small in general for liquid solutions. However, the designer must act on the flow configuration if it is desired to overcome the deleterious effects of the low molecular diffusivity.

Due to the importance and design challenges of the absorber, means to enhance absorber performance have long been of considerable interest. The enhancement methods can be classified into two categories, passive and active. Both are based on the same mixing concept but use different techniques to promote the mixing. Due to the increased complexity of active enhancement, most enhancement used today is still passive.

A literature survey of passive enhancement shows some advancement with time. As shown by Yih and Chen [1], and Miller and Perez-Blanco [2], wavy or turbulent flow is created by means of introducing extended surfaces, splashing, using additives, or simply increasing solution flow Reynolds number. However, no real new approaches to passive enhancement have been unearthed recently. The maximum

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NOMENCLATURE

C_p	specific heat
D	diameter
D_{AB}	mass diffusivity
f	frequency
h	heat transfer coefficient
i	enthalpy
k	thermal conductivity
L	length of absorber tubes
$\dot{m}$	mass flow rate
P	pressure
Pr	Prandtl number ($C_p\mu/k$)
$\dot{Q}$	heat flux
r	radius of absorber tubes
Re	Reynolds number ($4\Gamma/\mu_s$ for solution, VD/ν for coolant)
t	time
T	temperature
U	overall heat transfer coefficient
V	velocity
x	solution concentration
z	vertical distance from absorber solution inlet.

Greek symbols

α	thermal diffusivity
Γ	mass flow rate per unit
δ	film thickness
κ	mass transfer coefficient
μ	dynamic viscosity
ν	kinematic viscosity
ρ	density.

Subscripts

c	coolant bulk values
ci	coolant inlet conditions
i	inside side of absorber tubes
if	interface
ins	instantaneous values
mix	mixing
o	outside of absorber tubes
p	over a period of time
s	solution bulk values
si	solution inlet conditions
v	vapor
w	wall.

mass absorption rates reported at typical absorber conditions were in the order of 2.8×10^{-3} kg $\mathrm{m}^2 \cdot \mathrm{s}^{-1}$. In modeling the heat and mass transfer process in horizontal-tube-bundle-type absorbers, Andberg [3] used finite difference methods to solve the governing partial differential equations. Kirby [4] presented a one-dimensional falling film model taking into account droplet formation and fall for smooth and advanced tube surfaces. Generally, the new surfaces allow enhancements of up to 65% over smooth tubes, with maximum mass absorption rates of 4.2×10^{-3} kg $\mathrm{m}^2 \cdot \mathrm{s}^{-1}$. In real practice, chemical additives are often used for either corrosion inhibition or for heat and mass transfer enhancement. The additive effect is considered to stem from promotion of interfacial turbulence by surface tension gradients, also called the Marangoni effect. Sheehan and Perez-Blanco [5] found that the enhancement by using 2-ethyl-1-hexanol as the additive is typically about 30%.

When mixing is promoted mechanically, active enhancement is obtained. Swallow and Smith [6] presented a mechanically aided absorber comprising of several rotating disks semi-submerged in a solution trough. Due to disk rotation, the thin solution film formed on the disk surfaces can be constantly refreshed and mixed. Kostin and Gorshkov [7] studied the effect of mechanical vibrations on absorption heat and mass transfer enhancement. However, because the imposed vibrations failed to mix the interface fluids with the bulk effectively, the reported increase of mass transfer was only 15%. Instead of using liquid or vapor surfactants as additives, Lee [8] used lightweight magnetic particles driven by external magnetic fields to disturb a solution film formed on an inclined plate. The results showed a mass transfer rate of 2.5×10^{-2} kg $\mathrm{m}^2 \cdot \mathrm{s}^{-1}$. This is the maximum mass transfer rate reported to date in the open literature.

In searching for means of absorption enhancement, it is of interest to know the maximum absorption rate as a criterion for absorber performance evaluation. The objective of the paper is to develop a method to project the maximum absorption rates possible with active enhancement.

APPROACH

Every mass transfer enhancement technique, passive or active, consists of basically disturbing the film and causing mixing of the solution. Mixing of the solution can refresh the interface with the unsaturated solution from the bulk. The unsaturated solution then absorbs water vapor and becomes saturated or in equilibrium with the vapor pressure and the interface temperature. The amount of water vapor absorbed in the process is proportional to the degree of departure of the unsaturated solution from the equilibrium conditions. Therefore, if the refresh rate as well as the degree of departure increases, the mass absorption rate can be increased. The degree of departure of the unsaturated solution from the equilibrium conditions depends on how well the solution is mixed. To simplify the mixing process, it is simulated as a cyclic action of the solution with a certain frequency. For best enhancement, the mixing should be thorough and instantaneous or namely 'perfect'. At the beginning of each cycle the mixing makes the solution temperature and concentration distributions uniform across the film instantaneously, and the solution temperature and concentration are the average of the last cycle.

With the perfect mixing assumption, the maximum enhancement is derived by continuously increasing the mixing frequency until an asymptote of mass absorption rate is reached. It is reasonable to expect an upper enhancement limit, since the finite heat transfer coefficients of the absorber wall and the coolant do not allow infinite heat of absorption released to the film.

A complete solution for the absorption process calls for simultaneously solving the governing equations for heat transfer and mass transfer for both the solution and the coolant. Falling film turbulent motions usually seen in absorbers further heighten the complexity of the already complicated coupled heat and mass transfer problem. Therefore, using a simplified model to resolve the problem is inevitable. In doing so, a simplified one-dimensional (1-D) model for vertical tube absorbers has been developed as a first approximation. This model, being 1-D, accounts for variations only in the direction along the tube, yet all the absorber components and their thermal variables and properties are accounted for.

Since the mixing is assumed to be perfect, the temperature and concentration distributions across the film are uniform at the beginning of each mixing cycle. If the perfect mixing assumption is extended further to momentum transfer, the velocity distribution across the film would also be uniform at the beginning of each mixing cycle. This assumption is justified across the film except near the wall region where the velocity reduces to zero at the wall to satisfy the no-slip boundary condition. As far as the asymptote of mass absorption rate is concerned, the mixing frequency has to be large, and therefore, the time span between two consecutive mixing cycles is small. The distributions of velocity, temperature and concentration across the film should remain relatively uniform during a mixing cycle as the mixing frequency is high. In fact, to calculate the maximum enhancement it is not only necessary but also reasonable to use a 1-D approach.

Consider a vertical, smooth tube absorber using LiBr-water solution, which flows downward on the outside of the tube while the coolant flows countercurrently upward inside the tube, as shown in Fig. 1. Due to the heat of the absorption released at the interface, coupled with the heat transfer between the solution and the coolant, temperature variations along the longitudinal axis are developed in both fluids. The concentration of the solution decreases along the solution flow direction as a result of water vapor absorption.

When mixing is applied, the system is unsteady in nature in the interval between mixing. To avoid the

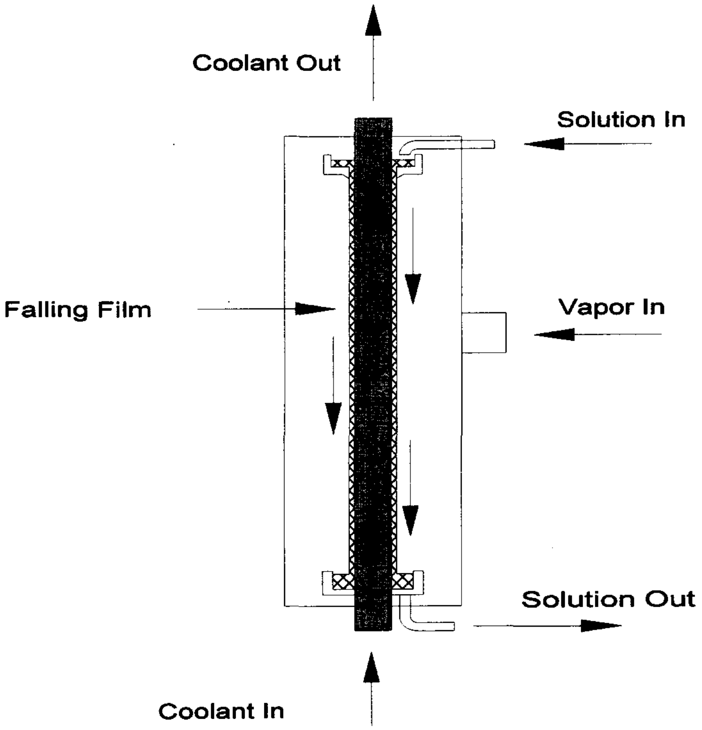

Fig. 1. Schematic of a falling-film absorber.

complexity of time variation inherent in the unsteady problem, the model is further simplified by averaging the heat and mass transfer coefficients with respect to time in a mixing cycle. Now that the problem is simplified to a 1-D, steady heat and mass transfer problem, a new treatment of this problem based on the model presented by Patnaik [9] has been developed.

GOVERNING EQUATIONS

The 1-D model for maximum enhancement is based on the following assumptions:

(1) 1-D, steady-state problem,
(2) equilibrium conditions at the solution–vapor interface at all time,
(3) constant coolant thermophysical properties,
(4) no heat transfer from the solution to the vapor occurs,
(5) no heat transfer in the longitudinal direction takes place,
(6) perfect mixing process,
(7) the solution film is treated as a semi-infinite medium for heat and mass transfer, and
(8) no non-condensable gases are present in the system.

Considering a thin slice of thickness Δz of an absorber tube as illustrated in Fig. 2, the solution flows down outside the tube and the coolant flows upwards inside the tube. The flows are separated by the tube wall. Three dependent variables, the coolant temperature, the solution bulk temperature, and the solution mass flow rate, and one independent variable, the vertical distance from the top of the absorber tube, will be considered.

Referring to the symbols in Fig. 2, the energy balance and mass balance on the solution side can be written as:

$$-\dot{Q}+\dot{m}_s i_s-(\dot{m}_s+\Delta\dot{m}_s)(i_s+\Delta i_s)+\Delta\dot{m}_v i_v = 0 \quad (1)$$

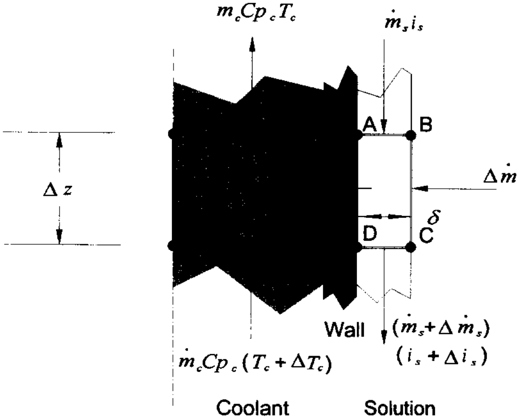

Fig. 2. A thin slice of an absorber tube.

$$\Delta\dot{m}_s = \Delta\dot{m}_v \quad (2)$$

$$\Delta\dot{m}_s = 2\pi(r+\delta)\,\Delta z\kappa_s\rho_s(x_s-x_{if}) \quad (3)$$

where δ is the film thickness. Because δ is normally very small compared to r, δ is negligible.

Similarly, the energy balance equation on the coolant side can be represented as:

$$\dot{Q}-\dot{m}_c C_{p_c} T_c+\dot{m}_c C_{p_c}(T_c+\Delta T_c) = 0 \quad (4)$$

where $\dot{Q}$ can be expressed in the conventional way by using the overall heat transfer coefficient U based on the outer surface of the tube as:

$$\dot{Q} = 2\pi r\,\Delta z U(T_s-T_c). \quad (5)$$

Substituting equations (2) and (5) into equation (1), and rearranging, we have

$$\frac{\Delta i_s}{\Delta z} = \frac{1}{\dot{m}_s}\left[\frac{\Delta\dot{m}_s}{\Delta z}(i_v-i_s)-2\pi r U(T_s-T_c)\right]. \quad (6)$$

Letting $\Delta \to 0$ yields the differential form of equation (6):

$$\frac{\mathrm{d}i_s}{\mathrm{d}z} = \frac{1}{\dot{m}_s}\left[\frac{\mathrm{d}\dot{m}_s}{\mathrm{d}z}(i_v-i_s)-2\pi r U(T_s-T_c)\right]. \quad (7)$$

The term on the left-hand side can be written as:

$$\frac{\mathrm{d}i_s}{\mathrm{d}z} = \left.\frac{\partial i_s}{\partial T_s}\right|_x \frac{\mathrm{d}T_s}{\mathrm{d}z}+\left.\frac{\partial i_s}{\partial x}\right|_{T_s}\frac{\mathrm{d}x}{\mathrm{d}z}. \quad (8)$$

From mass conservation of LiBr, the product $\dot{m}_s x$ is constant, which leads to

$$\frac{\mathrm{d}x}{\mathrm{d}z} = -\frac{x}{\dot{m}_s}\frac{\mathrm{d}\dot{m}_s}{\mathrm{d}z}. \quad (9)$$

Combining equations (7)–(9) yields

$$\frac{\mathrm{d}T_s}{\mathrm{d}z} = \frac{1}{\dot{m}_s\left.\frac{\partial i_s}{\partial T_s}\right|_x}\left[\frac{\mathrm{d}\dot{m}_s}{\mathrm{d}z}\left(i_v-i_s+x\left.\frac{\partial i_s}{\partial x}\right|_{T_s}\right)-2\pi r U(T_s-T_c)\right]. \quad (10)$$

Similarly, by letting $\Delta \to 0$, we have the differential forms of equation (3)

$$\frac{\mathrm{d}\dot{m}_s}{\mathrm{d}z} = 2\pi r\kappa_s\rho_s(x_s-x_{if}). \quad (11)$$

Note that δ is neglected in the equation. From the combination of equations (4) and (5), we have

$$\frac{\mathrm{d}T_c}{\mathrm{d}z} = \frac{-1}{\dot{m}_c C_{p_c}}\cdot 2\pi r U(T_s-T_c) \quad (12)$$

equations (10)–(12) represent the governing equations of the model. Each of those corresponds to one of the three dependent variables, T_s, $\dot{m}_s$ and T_c.

The boundary conditions are:

$$\text{at } z = 0, \quad T_s = T_{if} = T_{si}$$

$$x_s = x_{if} = x_{si}$$

$$\dot{m}_s = \dot{m}_{si}$$

$$\text{at } z = L, \quad T_c = T_{ci}.$$

Due to the relatively low thermal conductivity of the solution and high mixing frequencies, the thermal penetration depth on both the interface side and the wall side of the film is small compared to the film thickness in the interval between mixing. The heat transfer on both sides can be considered as the problem of unsteady-state heat transfer into a semi-infinite medium. From the solution given in Fahien [10], the heat flux at the interface is

$$\dot{Q}_{if} = \frac{k_s(T_{if} - T_s)}{\sqrt{\pi \alpha t}}. \tag{13}$$

From the definition of heat transfer coefficient, $\dot{Q}_{if} = h_{ins}(T_{if} - T_s)$, we obtain the instantaneous heat transfer coefficient h_{ins} as

$$h_{ins} = \frac{k_s}{\sqrt{\pi \alpha t}}. \tag{14}$$

To simplify the problem, the average heat transfer coefficient, h_s, over time t_p is given by integrating equation (14) from $t = 0$ to $t = t_p$ and dividing by t_p, which yields

$$h_s = \frac{2k_s}{\sqrt{\pi \alpha t_p}}. \tag{15}$$

This is also the heat transfer coefficient on the wall side, given the similarity of the thermal penetration problem.

The overall heat transfer coefficient is obtained as the inverse of the resultant of three resistances: the convective resistances on the coolant and solution sides, and the conductive resistance of the tube wall. Thus, we have

$$U = \left(\frac{r_o}{r_i}\frac{1}{h_c} + \frac{r_o}{k_w}\ln\frac{r_o}{r_i} + \frac{1}{h_s}\right)^{-1} \tag{16}$$

where h_c, the coolant side heat transfer coefficient, is obtained by applying Dittus–Boelter equation (11):

$$h_c = 0.023 \cdot Re_c^{0.8} \cdot Pr_c^{0.4} \tag{17}$$

since it is simple and reasonably accurate.

Similarly, the average mass transfer coefficient is given by

$$\kappa_s = 2\sqrt{\frac{D_{AB}}{\pi t_p}} \tag{18}$$

which also equals the overall mass transfer coefficient since it is assumed that there is no non-condensable gases in the system and the sole mass transfer resistance is on the solution side.

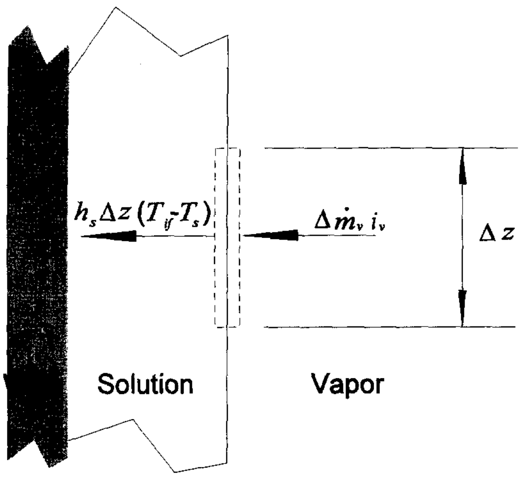

Fig. 3. Energy balance at the interface.

To obtain the liquid–vapor interface conditions, consider an infinitesimally thin control volume of length Δz enclosing the interface, as shown in Fig. 3. Performing an energy balance on the control volume yields

$$\Delta \dot{m}_v i_v = 2\pi(r + \delta)\,\Delta z h_s(T_{if} - T_s). \tag{19}$$

Substituting equation (2) and letting $\Delta \rightarrow 0$, we have

$$T_{if} = T_s + \frac{i_v}{2\pi r h_s}\frac{d\dot{m}_s}{dz}. \tag{20}$$

Again, the film thickness δ has been neglected.

From the interface temperature, assuming equilibrium conditions at the interface, we obtain the interface concentration as:

$$x_{if} = f(T_{if}, P). \tag{21}$$

The functional relationship in equation (21) is given by instance in *ASHRAE Handbook of Fundamentals* [12].

The three governing equations, equations (10)–(12), form a system of non-linear ordinary differential equations, which can be solved by using a fourth-order Runge–Kutta scheme. Since the boundary conditions are mixed, the solving procedure is performed using a standard shooting technique. By assuming a coolant outlet temperature, the computed coolant inlet temperature is compared to the known value and the criterion of convergence is set to 10^{-2}°C. If the criterion is not met, the downward integration is repeated with an improved coolant outlet guess based on a bisection technique, until convergence is established.

RESULTS

To approach practical conditions, typical values found in commercial chillers are used. A single-effect absorption chiller typically operates at about 6 mmHg absorber pressure using 29.5°C (85°F) cooling water flowing at a velocity not exceeding 2.74 m s^{-1} (9 fps).

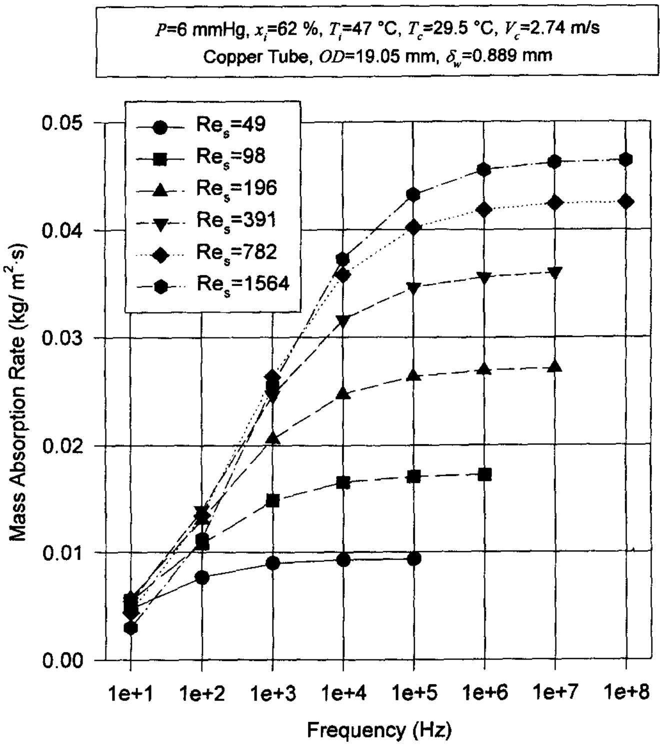

Fig. 4. Effect of mixing frequency and inlet solution Reynolds number on mass absorption rate.

Copper smooth tubes with 0.01905 m (3/4″) OD are the most widely used absorber tubes. Equilibrium solution with a concentration of 62% by weight of LiBr is a common solution inlet condition. In addition, a tube length of 1.5 m is selected for the calculation.

Figure 4 shows the effect of mixing frequency (f_{mix}) on mass absorption rate for some selected inlet solution Reynolds numbers (Re_s) which is defined as $4\Gamma/\mu_s$, where Γ is the solution mass flow rate per unit film width and μ_s is the dynamic viscosity of the solution. The higher the Reynolds number, the higher the asymptotic mass absorption rate and the higher the mixing frequency required for the mass absorption rate to become asymptotic.

Note that in Fig. 4, Re_s is increased by a factor of two. However, the increase of the asymptotes is not proportional to the increase of Re_s. The enhancement becomes smaller as Re_s increases. Therefore, it is possible to reach an asymptotic value if Re_s is continuously increased. This point is shown graphically by the solid curve in Fig. 5. This curve is constructed by connecting the asymptotic mass absorption rates at various Re_s. As Re_s increases, the curve levels off and reaches a value of 0.049 kg $\mathrm{m}^2 \cdot \mathrm{s}^{-1}$. Since this is an asymptotic value as both Re_s and f_{mix} approach infinity, it is the maximum enhancement possible for typical absorption chillers.

The solid curve in Fig. 5 shows the effect of inlet solution Reynolds number on the asymptotic mass absorption rate. Each point on the curve is calculated by setting an inlet solution Reynolds number and then increasing the mixing frequency until the asymptote is reached. As shown in the figure, the asymptotic mass absorption rate increases sharply with increasing solution Reynolds number at low Reynolds number. At a Reynolds number of 1000, the asymptotic mass absorption rate reaches 90% of the theoretically possible maximum mass absorption rate at assumed conditions, about 0.049 kg $\mathrm{m}^2 \cdot \mathrm{s}^{-1}$.

In addition to the mass absorption rate, the concentration difference between the solution inlet and the outlet is also an important parameter for absorbers. High concentration differences in an absorber can reduce the solution flow rates and therefore reduce the cycle recirculation loss. The variation of the concentration difference vs. the inlet solution Reynolds number for the typical absorber is also shown in Fig. 5 by the dashed curve. The difference is calculated using the results from the asymptotic mass absorption rate calculation used to construct the solid curve. It is obvious that the two curves in Fig. 5 have opposite trends. However, since both the concentration difference and the mass absorption rate are sought to be high, a compromise must be found. The intersection of the two curves may suggest a possible optimum operating point for the absorber, which is at $Re_s = 360$. The corresponding mass absorption rate

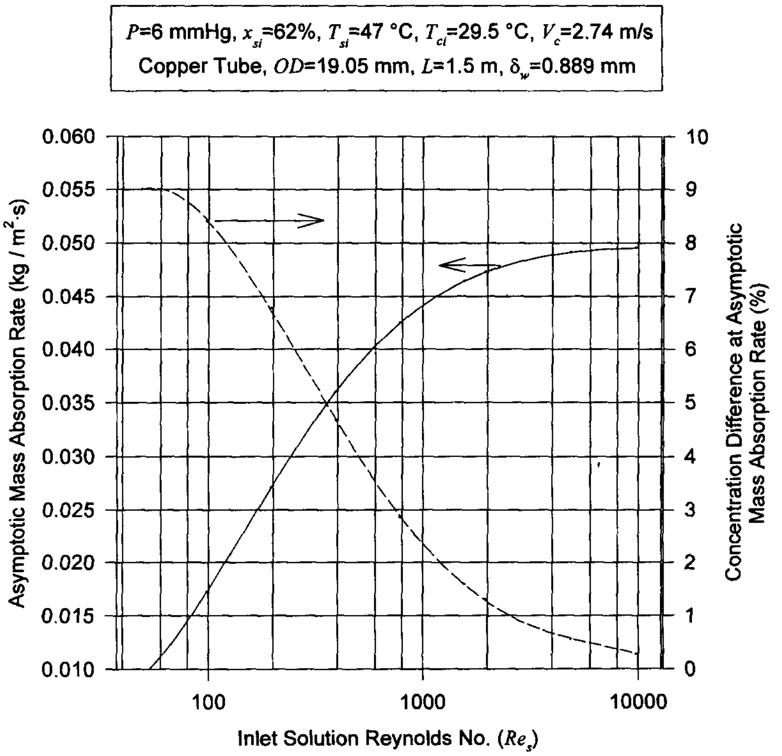

Fig. 5. The effects of inlet solution Reynolds number on asymptotic mass absorption rate and solution concentration difference.

and concentration difference are $0.035 \text{ kg m}^2\cdot\text{s}^{-1}$ and 5%, respectively.

Consider the case for $Re_s = 391$ and $f_{\text{mix}} = 1000$ Hz (a mechanically achievable frequency) in Fig. 4. The mass absorption rate is $0.0256 \text{ kg m}^2\cdot\text{s}^{-1}$ and the corresponding concentration difference is 3.27%. If the typical mass absorption rate of $0.0027 \text{ kg m}^2\cdot\text{s}^{-1}$ is used as the baseline value, a maximum enhancement factor of 9.5 is derived. This suggests that the performance of current absorbers is well below what it possibly could be. Therefore, by using enhancement techniques, an order of magnitude of enhancement in the mass absorption rate is achievable. However, it is difficult to produce high mixing frequencies required to achieve such a high mass absorption rate by passive techniques. Active techniques are therefore more likely to be adopted for high performance absorbers.

CONCLUSIONS

The present study of mass transfer enhancement in LiBr absorbers has led to the conclusions that to achieve enhancement the solution film must be mixed and that the mixing must be capable of exchanging the interface fluids with the bulk. Active enhancement can effectively disturb the solution at high mixing frequencies and therefore enhancement factors exceeding 10 are possible. However, the increased complexity of active enhancement has turned its development into a real challenge. In addition to high performance, a good active enhancement technique has to be cost effective, long in life expectancy, maintenance free, and easy to implement.

A 1-D model to calculate the mass absorption rate for maximum enhancement has been developed. The model takes into account all relevant parameters such as temperatures, pressures, concentrations, mass flow rates, and geometry, providing a good approach to absorber performance evaluation. A system of three ordinary differential equations was solved by using a fourth-order Runge–Kutta scheme. Results show that for typical absorber operating conditions the mass absorption rate can be as high as $0.049 \text{ kg m}^2\cdot\text{s}^{-1}$, which is the theoretical maximum for mixing technology. If the mixing frequency is restricted below 1000 Hz, a mechanically achievable mixing rate, a mass absorption rate of $0.0256 \text{ kg m}^2\cdot\text{s}^{-1}$ with a corresponding concentration difference of 3.27% is obtained. This mass absorption rate is about an order of magnitude larger than that of the absorbers in commercial machines. Therefore, the potential for developing high performance absorbers by active methods appears to be promising.

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