

MASS TRANSFER IN HETEROGENEOUS SYSTEM WITH CHEMICAL REACTION

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(Received 15 April 1980)

Abstract— Mass transfer associated with chemical reaction and gaseous bubbles in heterogeneous system is investigated experimentally in the present paper. It is shown that the j -factor correlation similar to Chilton–Colburn correlation for mass transfer can be applied. For calcite–HCl solution system, the correlation is obtained: $j^* = 118Re^{-1}$, for $Re < 1.4 \times 10^4$, and $j^* = 0.189Re^{-1/3}$, for $14000 < Re < 10^5$. It is also found that the transition point is shifted to at Reynolds number near 14000.

NOMENCLATURE

| | |
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| C_A | concentration of HCl solution [mole l ⁻¹]; |
| D_{AB} | diffusivity of HCl in water [cm ² s ⁻¹]; |
| d_e | hydraulic diameter of the rectangular channel [cm]; |
| H | height of rectangular channel [cm]; |
| j^* | modified j -factor ($= Sh^*/ReSc^{1/3}$); |
| \bar{k} | overall rate constant [cm s ⁻¹]; |
| k_f | overall film conductance [cm s ⁻¹]; |
| k_s | surface reaction conductance [cm s ⁻¹]; |
| k | specific overall rate constant [cm s ⁻¹]; |
| L | length of specimen [cm]; |
| ν | kinematic viscosity of HCl solution [cm ² s ⁻¹]; |
| r_A | overall reaction rate of HCl [mole cm ⁻² s ⁻¹]; |
| r_C | overall reaction rate of calcite [mole cm ⁻² s ⁻¹]; |
| Re | Reynolds number of main stream (vd_e/ν); |
| Sc | Schmidt number (ν/D_{AB}); |
| Sh^* | modified Sherwood number ($= kd_e/D_{AB}$); |
| v | mean velocity across the rectangular channel [cm s ⁻¹]; |
| W | width of test section [cm]. |

I. INTRODUCTION

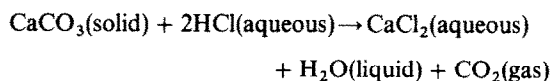
MASS transfers associated with chemical reactions in heterogeneous systems are exceedingly important phenomena in today's technology, especially in chemical and process engineering. Numerous empirical correlations concerning mass-transfer coefficient for fluid–solid exchange without the presence of the third phase and chemical reaction have been published over many years such as the famous Chilton–Colburn correlation, etc. [1–3]. For fluid–solid mass transfer with chemical reaction, it was found that either the mass-transfer or the chemical-reaction rate can be the controlling step in this simultaneous process; more frequently, neither rate completely dominates [4–6].

In general, treatment of simultaneous mass transfer

and chemical reaction is extremely complicated especially at the presence of third phase such as gaseous bubbles. Unfortunately, a lot of liquid–solid mass transfers in practical applications are found to be accompanied with chemical reactions and with gaseous products. Gaseous products would form bubbles within the liquid phase and induce agitating effect to the main stream by the bubble uprising motion and affects the overall mass-transfer rate. The mechanism is so complicated that only little work has been done on this subject up to date. To understand the detailed mechanism, an experiment is carried out in the present work to investigate the liquid–solid mass transfer with chemical reaction and gaseous products.

II. EXPERIMENT

Calcium carbonate (calcite) is selected as the solid reactant and the hydrochloride aqueous solution as the liquid phase in the experiment. The basic chemical reaction of these two reactants is



in which the carbon dioxide gaseous product is generated and forms bubbles in the liquid phase. In this reaction, shrinking unreacted core model can be applied since the solid is not porous and no ash forms [4]. Therefore, two resistances will be encountered in controlling the overall mass-transfer rate; namely, the liquid film resistance and the surface reaction resistance. The following three steps which occur in succession can be visualized for this kind of reaction.

1. Transport of reactant A (HCl) from liquid main stream through the liquid film to the surface of the solid by diffusion and convection.
2. Reaction on the surface between reactant A and solid (CaCO₃).
3. Transport of reaction products from the surface of solid through the liquid film back into the main stream by diffusion and forced convection accompanied with bubbles.

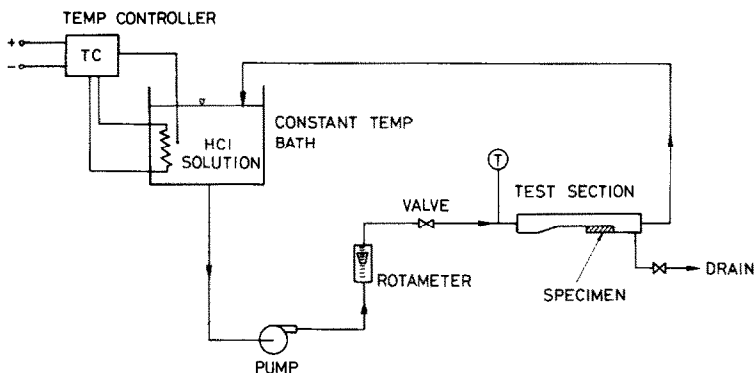


FIG. 1. Schematic diagram of apparatus.

The reaction rate thus can be represented by the first order equation:

$$r_c/2 = r_A = \bar{k}C_A = C_A/(1/k_f + 1/k_s) \quad (1)$$

where r_c is the overall reaction rate of calcite, r_A is the reaction rate of HCl, \bar{k} is the overall rate constant, C_A is the concentration of HCl solution, $1/k_f$ is the overall film resistance, and $1/k_s$ is the surface reaction resistance. Equation (1) can be written as

$$r_c = kC_A \quad (2)$$

where $k = 2\bar{k} = 2/(1/k_f + 1/k_s)$. k is the specific overall rate constant with respect to the solid reactant.

To investigate the mass transfer, an experimental equipment was set up as shown in Fig. 1. Hydrochloride aqueous solution is pumped through the acrylic rectangular channel (test section) where the solid phase (CaCO_3) is placed at the bottom. The inlet section was designed long enough such that fully developed flow can be obtained before entering the test section. Since Schmidt number Sc and Reynolds number Re play a very important role in mass-transfer phenomena, the experiment was performed using different concentrations of hydrochloride solution (0.5–2.0 N) at different temperatures (20–60°C) which were controlled by a temperature controller in the

bath. The flow rate was controlled by adjusting the valve and measured by a rotameter which was carefully calibrated to within $\pm 3\%$ error. The mean velocity across the test section then can be determined.

To eliminate the edge effect induced by the side walls of the test section, the test specimen (CaCO_3) was placed at the bottom with 1 cm distance apart from the side walls (see Fig. 2) and acrylic blocks were fulfilled between the specimen and the side wall such that a smooth surface coplanar with the specimen was kept at the bottom of the test section. Furthermore, five sides of the specimen were painted with non-dissolved paint except the side facing the main stream so that the mass transfer only occurred at the upper solid surface. Reaction rate of solid r_c was then determined by measuring the weight loss of calcium carbonate before and after flushed in the acid stream at a given time interval. The overall rate constant k can also be determined according to equation (2).

To calculate the dimensionless groups for correlation, the diffusivity of hydrochloride acid in water D_{AB} was computed using Wilke and Chang's data [7, 8] and Powell, Roseveare and Eyring's data [6] to account for the effects of temperature and concentration. The viscosity of hydrochloride acid solution for concentrations below 10% in weight can be

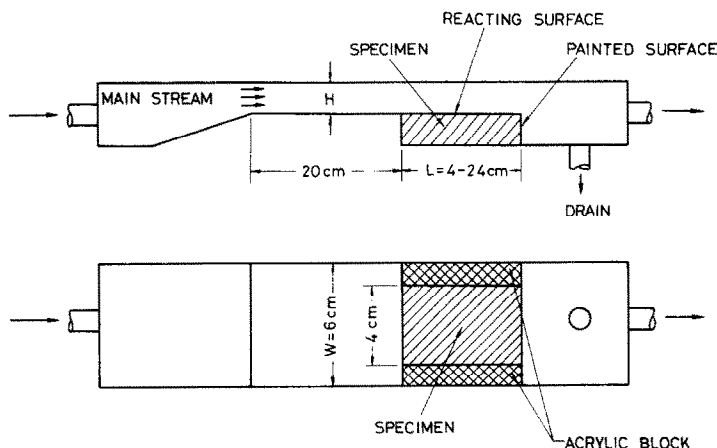


FIG. 2. Test section.

approximated by that of water according to Treybal [9].

III. RESULTS AND DISCUSSIONS

For mass transfer in homogeneous systems without chemical reaction, the Sherwood number, which is defined based on the mass transfer coefficient of the fluid phase, is always used for the correlation of experimental results. Now, for mass transfer in heterogeneous system with chemical reaction, intuitively it is reasonable to introduce a modified Sherwood number, Sh^* ($= kd_e/D_{AB}$), which is defined based on the specific overall rate constant k , and a modified j -factor, j^* , which is defined based on Sh^* . Through this treatment, a correlation similar to the form of the Chilton–Colburn correlation might be expected.

The experimental data are correlated using modified Sherwood number, Sh^* , Schmidt number, Sc , and Reynolds number (vd_e/ν) where v is the mean velocity of the main stream at the test section and d_e is the hydraulic diameter of the test section. It is very interesting to note from Fig. 3 that a correlation using the modified j -factor, j^* , and being similar to the form of the Chilton–Colburn correlation can be obtained very well. An empirical relation, equation (3), also can be derived from the data and compared with the Chilton–Colburn relation [10] as shown in Fig. 3.

$$j^* = \begin{cases} 118Re^{-1} & Re < 14000 \\ 0.189Re^{-1/3} & 14000 < Re < 10^5 \end{cases} \quad (3)$$

The present correlation is valid only for $50 < Sc < 400$ and $L/H < 12$, as far as the available experimental data is concerned. Thus we can see that the j -factor correlation which is generally used for homogeneous systems also can be applied to the mass transfer with chemical reaction and bubbles in heterogeneous sys-

tem. The major differences, however, are the shift of the transition point at Reynolds number from 2100 for homogeneous system to 14 000 for the present heterogeneous system and the slope after the transition point. The present heterogeneous system has a little higher slope. And, the mass-transfer rate is apparently larger for heterogeneous system. This is possibly due to the bubble agitating effect and the chemical reaction. Since the mass transfer mechanism near the reacting surface is extremely complicated, it is very difficult exactly to explain the phenomenon of the shift of the transition point in details simply from the measurements of the overall mass-transfer rate in the present experiment. But it can be seen from Fig. 4 that the present result implies that at Reynolds number larger than 14 000 the overall mass-transfer rate tends to be film resistance controlled. At Reynolds number less than 14 000, the overall mass-transfer rate is probably surface reaction controlled since the modified Sherwood number or the overall rate constant, k , are independent of Reynolds number, i.e. $k \approx k_s$, where k_s is the surface reaction conductance or chemical reaction rate constant that is only a function of chemical reaction mechanism. For Reynolds number larger than 14 000, the situation becomes more complicated. At this case, the modified Sherwood number or the overall rate constant, k , starts to increase with Re . It seems that the overall mass-transfer rate is film resistance controlled, i.e. $k \approx k_f$, where k_f apparently depends on Reynolds number. These might be due to the severe agitation and entrainment motion of bubbles and the interactions with the turbulent eddies from the main stream. A new theoretical model which accounts for the bubble dynamics, molecular diffusion process, chemical reaction, and fluid dynamics etc. as well as a new experimental technique would be required in solving this problem. At last, it should be noted that

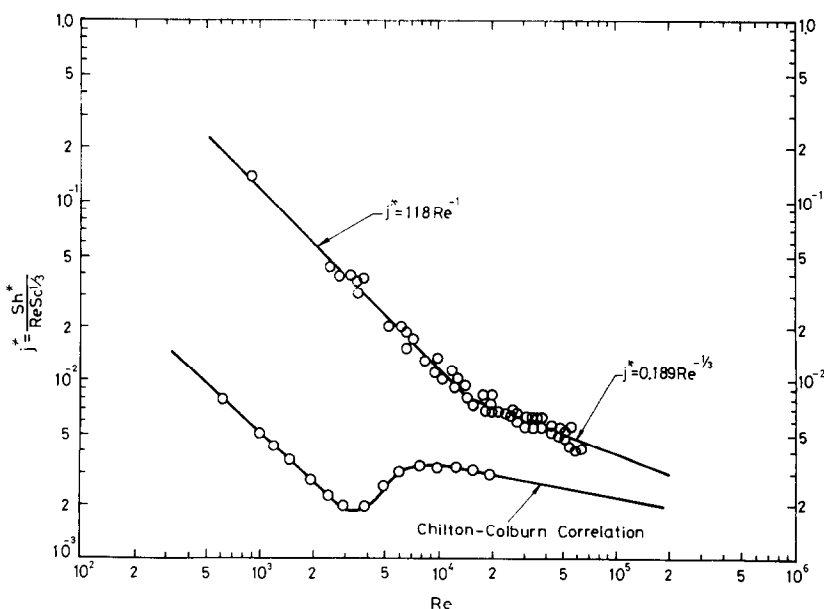


FIG. 3. Modified j -factor correlation and comparison with Chilton–Colburn correlation.

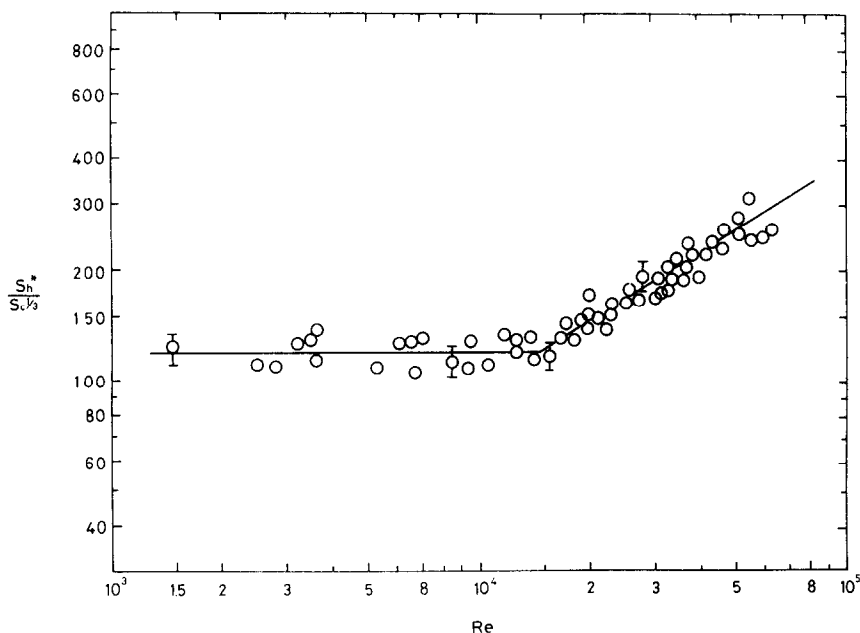


FIG. 4. Correlation of modified Sherwood number.

the effect of bubble dynamics is ignored in the present studies although the bubble sizes and formation frequency would play important roles in bubble agitation or mass-transfer rate. Therefore, the present correlation would not be universal for all heterogeneous systems but only holds for calcite-HCl solution system. However, the validity of the form of j -factor correlation with some modification for heterogeneous system is justified here and can be extended to the other heterogeneous systems.

IV. CONCLUSIONS

Mass transfer associated with chemical reaction and gaseous bubbles in heterogeneous system is investigated experimentally in the present paper. The results show that the j -factor correlation for mass transfer in homogeneous system can be applied to heterogeneous system with some modification in defining the j -factor. For calcite-HCl solution system, the correlation is obtained, equation (3). It is also shown that the transition Reynolds number is shifted to near 14 000 for calcite-HCl solution system. Since the bubble dynamics has been ignored because of its complexity, the present correlation is not universal but only valid for calcite-HCl solution system. However, the validity of the form of j -factor correlation for heterogeneous system has been justified and can be extended to other heterogeneous systems in which the transition point

and the slopes might be changed. Further investigations are still required.

Acknowledgement — The author would like to express his gratitude to Dr. M. S. Gon for his discussions and to Mr. S. T. Wang and Mr. Y. M. Chen for their assistance in the experiment. This work was supported by the Chinese Petroleum Co.

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TRANSFERT MASSIQUE DANS UN SYSTEME
HETEROGENE AVEC UNE REACTION CHIMIQUE

Résumé—On étudie expérimentalement le transfert massique associé avec une réaction chimique et des bulles gazeuses dans un système hétérogène. On montre que la formule du facteur j pour le transfert massique, semblable à celle de Chilton–Colburn, peut être appliquée. Pour la solution calcite-HCl, on obtient $j^* = 118 Re^{-1}$ pour $Re < 1,4 \cdot 10^4$ et $j^* = 0,189 Re^{-1/3}$ pour $14\,000 < Re < 10^5$. On trouve aussi que le point de transition est déplacé vers un nombre de Reynolds proche de 14 000.

STOFFÜBERGANG IN EINEM HETEROGENEN SYSTEM MIT
CHEMISCHER REAKTION

Zusammenfassung — In der vorliegenden Arbeit wird über Experimente zum Stoffübergang bei chemischer Reaktion in einem heterogenen System in Anwesenheit von Gasblasen berichtet. Es wird gezeigt, daß die Korrelation mit dem j -Faktor ähnlich der Chilton–Colburn-Korrelation auf den Stoffübergang angewendet werden kann.

Für das Lösungssystem Kalzit-HCl erhält man die Korrelation:

$$j^* = 118 Re^{-1}, \quad \text{für } Re < 1,4 \times 10^4$$

und

$$j^* = 0,189 Re^{-1/3}, \quad \text{für } 14\,000 < Re < 10^5.$$

Außerdem wurde festgestellt, daß sich der Übergangspunkt zu einer Reynolds-Zahl in der Nähe von 14 000 verschiebt.

МАССОПЕРЕНОС В НЕОДНОРОДНОЙ СИСТЕМЕ ПРИ ХИМИЧЕСКОЙ РЕАКЦИИ

Аннотация — Экспериментально исследуется перенос массы при химической реакции в неоднородной системе, содержащей пузырьки газа. Показано, что перенос массы можно описывать с помощью корреляционного коэффициента j_0 по аналогии с зависимостью Чилтона–Колберна. Такое соотношение выведено для системы кальцит-HCl, для которой $j^* = 118 Re^{-1}$ при $Re < 1,4 \times 10^4$ и $j^* = 0,189 Re^{-1/3}$ при $14\,000 < Re < 10^5$. Показано также, что точка перехода соответствует $Re \approx 14\,000$.