PENETRATION MODEL FOR GAS ABSORPTION WITH REACTION IN A SLURRY CONTAINING FINE INSOLUBLE PARTICLES

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ABSTRACT

A pseudo-homogeneous penetration model describing the mass transfer of a gas to a slurry containing non-soluble reacting or adsorbing particles is presented. This numerical model takes into account the finite reaction/adsorption capacity of the particles. The consequences of this finite capacity on the enhanced absorption are demonstrated for the absorption of hydrogen in metal hydride slurries. Experimental enhancement factors for this system are evaluated and compared to the model predictions. A critical Hatta number has been derived above which saturation of the solid occurs resulting in decreased enhancement factors. The mass transfer of a gas into a slurry with adsorbing particles is a similar problem. For the regime of mass transfer limitation to the particles with a linear adsorption isotherm the enhanced adsorption is discussed.

KEYWORDS

Gas absorption enhancement; slurry; fine insoluble particles; limited adsorption capacity of particles; penetration model.

INTRODUCTION

Small particles, suspended in a liquid can play a role in the enhancement of gas absorption if they have catalytic activity or if they represent a source of soluble reactant. A recent review on this subject has been given by (Beenackers & Van Swaaij, 1985). We have also recently reported (Ptasiński, 1985) that enhancement of gas absorption may occur with particles forming a non-soluble reactant.

Theoretical models describing the enhanced absorption of gas in liquid with suspended solids which have been developed for systems with soluble solids (Sada, 1984) and systems with solids as a catalyst (Alper, 1980; Jamakiraman, 1985; Kralj, 1984) usually considered stationary transport through the diffusion film containing particles smaller than the film thickness. Only (Uchida, 1981) treated the problem of absorption with instantaneous reaction with soluble solids with the penetration theory, but like for gas-liquid systems he has found almost no difference with the film theory. In case of a system gas-liquid-insoluble solid with a limited adsorption or reaction capacity no stationary models can be applied (Ptasiński, 1986), because after a certain contact time the particles near the interface can become completely converted. During absorption a growing layer of slurry with non-reactive particles can be formed starting at the interface. Neglecting this effect leads to an over-estimation of the overall reaction rate in the film. To simulate this situation therefore only instationary models can be used for this problem. In the present contribution a pseudo-homogeneous penetration model is developed. The absorption of hydrogen in a slurry of very small hydride forming alloy particles and the absorption of gases in slurries of adsorbing particles, is used to demonstrate the theory.

MASS TRANSFER MODEL

We will describe mass transfer in the slurry phase by means of Higbie's penetration model, while we will neglect the gas phase mass transfer resistance. It is not difficult to incorporate the gas phase resistance as was shown elsewhere (Cornelisse, 1980).

As stated before the reason for using the penetration model is that only an instationary model can give realistic results in describing mass transfer in a slurry with particles with limited capacity for adsorption and reaction. The kinetics of the reversible reaction between the absorbed gas and the solid particles forming a product in the solid state will be represented by:

When the reaction (or adsorption) rate of A on the solid surface with S is very fast compared to the mass transfer rate of A to the solid surface then the rate of disappearance of A from the liquid will be limited by mass transfer to the particles. Assuming this is valid the phenomena of simultaneous diffusion plus mass transfer to the particle in the liquid near the interface are described as follows:

- for the absorbing component the mass balance reads:

$$\frac{\partial A}{\partial t} = D_A \frac{\partial^2 A}{\partial x^2} - k_{1s} a_s (A - A_S) \quad (1)$$

- the product mass balance:

$$\frac{\epsilon_S}{(1-\epsilon_S)} \frac{\partial P}{\partial t} = k_{1s} a_s (A - A_S) \quad (2)$$

with A_S as the concentration of A in the liquid at equilibrium with the solid surface concentration.

Accordingly, in terms of Higbie model, boundary conditions are

$$\left. \begin{array}{l} \text{for } t = 0 ; x \geq 0 \\ t \neq 0 ; x = \infty \end{array} \right\} \begin{array}{l} A_S = \bar{A} \\ P = \bar{P} \end{array} \quad (3)$$

The enhancement factor E is defined as the average flux of A as compared to the situation with similar but inert particles:

$$E = \frac{1}{\tau} \int_0^\tau D_A \left. \frac{\partial A}{\partial x} \right|_{x=0} dt / \left[2 \sqrt{\left(\frac{D_A}{\pi \tau} \right)} (A_{x=0} - A_{x=\infty}) \right] \quad (4)$$

where τ is the contact time of the stagnant element with the gas phase.

A special kind of Hatta number can be defined:

$$Ha' = \sqrt{(k_{1s} a_s D_A / k_1^2)} \quad (5)$$

$$\text{in which } k_1 = 2 \sqrt{\left(\frac{D_A}{\pi \tau} \right)} \quad (6)$$

It should be realised of course that $k_{1s} a_s$ in this case is not a reaction rate constant but a rate constant of a physical process i.e. mass transfer to the particle surface. For the sake of convenience in the numerical treatment of the system the equations have been transformed into a dimensionless form. After rearrangement of the original set of eqns (1)-(3) a new set of dimensionless equations can be denoted (7)-(9), which is suitable for numerical treatment.

$$\frac{\partial a}{\partial \theta}(\theta, z) = \frac{4}{\pi} \frac{\partial^2 a}{\partial z^2}(\theta, z) - M(\theta, z) [a(\theta, z) - e(\theta, z)] \quad (7)$$

$$\frac{\partial p}{\partial \theta}(\theta, z) = \frac{M}{R}(\theta, z) [a(\theta, z) - e(\theta, z)] \quad (8)$$

boundary conditions:

$$\left. \begin{array}{l} \text{for } \theta = 0 ; z \geq 0 \\ \theta \neq 0 ; z = \infty \end{array} \right\} \begin{array}{l} a = \bar{a} \\ p = \bar{p} \end{array} \quad (9)$$

The numerical method for solving the parabolic differential equations is essentially the three-point backward scheme by Baker & Oliphant. We refer for an extensive description, explanation of the discretization technique, the time-, place transformations, the filling of the tridiagonal band matrix and the method for solving band matrices to a previous publication (Cornelisse, 1980).

ABSORPTION OF HYDROGEN IN METAL HYDRIDE SLURRY

Description of the system

Initially we developed the present model to describe the absorption of hydrogen in a slurry of metal hydride forming particles ($\bar{d}_p = 7 \mu\text{m}$) and oil. Metal hydrides are reaction products of hydrogen with various metal alloys like LaNi_5 , FeTi and Mg_2Ni , etc. These alloys have the property that they can react fast with hydrogen forming a metal hydride. During a great part of the pressure/composition isotherm the hydrogen pressure in equilibrium with the hydride remains almost constant, resulting in a constant hydrogen concentration at the particle's surface, see Fig. 1 (Ptasinski, 1983, 1985).

Much attention has been paid to the concentration process and storage of hydrogen with the aid of hydrides in the form of packed beds. Several problems related to packed bed operation such as poor heat transport, embrittlement and entrainment of fines, discontinuous operation, etc could be solved by the application of hydrides in a slurry system and this concept is tested in our laboratory (Beenackers, 1982, 1983; Ptasinski, 1983, 1985).

Experimental data concerning reaction rates of hydrogen with a dry hydride, LaNi_5 ($T > 25^\circ\text{C}$) (Goodeil, 1983), show that at normal operation conditions the reaction rate is extremely fast. For particles in a liquid it will be several decades greater than the mass transfer rate, assuming $\text{Sh} = 2$. This means that for not completely converted particles over the whole diffusion layer the concentration of H_2 at the particle's interface will remain at equilibrium, $A_S = A_{eq}$, and the process will indeed be mass transfer limited. When a particle reaches its maximum loading, the reaction rate rapidly decreases to zero, because then A_S approaches A (see eq. 1). In mathematical terms this is idealized by setting at a certain position the flux to the particles to zero as soon as the maximum particle loading of hydrogen is reached.

Fig. 1. Pressure composition isotherm at 20°C and 70°C for LaNi_5 .

Fig. 2. Concentration profiles of H_2 and hydrides at $t = \tau$ vs. Ha' . $\text{H}_{2,g} = 500$, $\text{H}_{2,g,eq} = 80 \text{ mole/m}^3$, $\epsilon_S = 0.06$, $\text{Ha}'_0 = 7.11$, $m = 0.08$, $\Delta P_{\max} = 3.61 \cdot 10^4 \text{ mole/m}^3 \text{ solid}$.

The particles nearest to the interface are the first to be completely converted. For these particles we may write:

$$\text{at } x = 0 \quad \left. \frac{\partial P}{\partial t} \right|_{x=0} = \left(\frac{1-\epsilon_S}{\epsilon_S} \right) k_{1s} a_s (m A_g - A_{eq}) \quad (10)$$

integration leads to:

$$P_{\max} - \bar{P} = \left(\frac{1-\epsilon_S}{\epsilon_S} \right) k_{1s} a_s (m A_g - A_{eq}) \tau = \frac{4 \text{Ha}'^2}{\pi} (m A_g - A_{eq}) \left(\frac{1-\epsilon_S}{\epsilon_S} \right) \quad (11)$$

We now define Ha'_0 as the smallest Hatta' number where the first layer of particles is completely converted at the end of the package interface residence time τ .

$$\text{Ha}'_0 = \left(\frac{P_{\max} - \bar{P}}{m A_g - A_{eq}} \frac{\epsilon_S}{1-\epsilon_S} \frac{\pi}{4} \right)^{0.5} \quad (12)$$

Comparison of the experimental Hatta number and this critical Hatta number indicates, whether or not the enhancement factor is influenced by complete conversion.

Results hydrogen absorption simulations

We will present the results of the computer calculations for some typical examples of the absorp-

Fig. 3. E vs. Ha' at different volume fractions of solids. $\text{H}_{2,g} = 200$, $\text{H}_{2,g,eq} = 80 \text{ mole/m}^3$, $m = 0.08$, $\Delta P_{\max} = 3.61 \cdot 10^4 \text{ mole/m}^3 \text{ solid}$.

Fig. 4. E vs. Ha' for different driving forces $= m(\text{H}_{2,g} - \text{H}_{2,g,eq})$. $\epsilon_S = 0.06$, $m = 0.08$, $\Delta P_{\max} = 3.61 \cdot 10^4 \text{ mole/m}^3 \text{ solid}$.

tion of H_2 in $LaNi_5$ -oil slurries. The concentration profiles of H_2 and hydride in a typical package at the interface at $t=\tau$ are shown in Fig. 2. The profiles show the effect of a converted layer on the concentration profile of hydrogen. When the hydrogen concentration in the solids (P) has not reached its maximum (P_{max}), the H_2 -profile at $t=\tau$ will remain the same independent of the Ha' -number. If Ha' is greater than Ha'_C , H_2 only reacts with particles after it has diffused through an inert suspension layer resulting in higher local concentrations of free H_2 . In Fig. 3 the enhancement factor is plotted against the Ha' -number for several solid concentrations. As follows from eq. (12) the Ha'_C -value will increase with increasing P_{max} . This is in agreement with the results given in Figure 3. Until Ha'_C is reached, the enhancement corresponds with the simple penetration theory solution. If Ha' is greater than 2 but smaller than Ha'_C , the enhancement factor is equal to Ha' : $E = Ha'$ if $2 < Ha' < Ha'_C$. Above Ha'_C the increase of E with Ha' will start to decline until ($Ha' = 3 Ha'_C$) an almost constant value of E is reached. Varying the driving force of absorption, Ha'_C will change proportionally to the reciprocal root of the driving force. Qualitatively this means, the effect of larger driving force results in higher concentrations of H_2 in the liquid, which cause higher fluxes to the particles, and they will become faster completely loaded. This effect of lower enhancement factors as a result of higher physical absorption fluxes (at $Ha' > Ha'_C$) is shown in Fig. 4. If a completely loaded layer occurs, the dependence of E with the driving force is clearly shown

Fig. 5. E vs. driving force for different Ha' . $\epsilon_S = 0.06$, $m = 0.08$, $\Delta P_{max} = 3.61 \cdot 10^4$ mole/m³ solid.

Fig. 6. E vs. bulk concentration hydride, $\bar{p}$ for different Ha' . $\epsilon_S = 0.06$, $m = 0.08$, $m(H_{2,g} - H_{2,g,eq}) = 9.6$, if $P_{max} - P = 3.0$ then $Ha'_C = 13.73$.

in Fig. 5. For a certain Ha' -number now a critical driving force can be defined, proportional to P_{max} and $1/Ha'^2$. Higher driving forces than the critical driving force for absorption result in decreased E -values.

Fig. 6 gives an impression what will happen if at certain Ha' -values the bulk loading of hydride, $\bar{P}$ is increased. Above Ha'_C , E will almost instantly decline with $\bar{P}$. Assuming mass transfer to the particle can be calculated by $Sh = 2$, E has been determined as a function of d_p for two k_1 -values. The mass transfer rate constant becomes:

$$k_{1s}a_s = 2 D_A/d_p * 6\epsilon_S/d_p * (1 - \epsilon_S) = 12 D_A\epsilon_S/d_p^2 * (1 - \epsilon_S) \quad (13)$$

and Ha' becomes proportional to $1/d_p$. Figure 7 shows that at high k_1 -values only with very small particles diffusion resistance can be demonstrated. At d_p -values larger than $d_{p,c}$ (from Ha'_C , k_1) the enhancement factor increases with $1/d_p$ (if $Ha' > 2$).

Comparison with experimental results.

In a stirred high-pressure autoclave we measured for flat interface conditions the absorption rate of hydrogen in $LaNi_5$ -oil slurries. By correcting for diffusion coefficients we calculated the physical absorption rate of hydrogen from the physical rates of absorption of an inert gas in the slurry. Experimental details are given elsewhere (Ptasinski, 1983, 1985). From these experiments the enhancement factors can be calculated.

TABLE 1 Adsorption of H_2 in 5.8 vol % $LaNi_5$ -oil Slurry. Experimental conditions: hydrogen pressure 26 bar, $\Delta P_{max} = 38.8 \cdot 10^3$ mol/m³ solid, $d_p = 7 \cdot 10^{-6}$ m, stirrer speed 400 rpm.

T, °C	$k_1 \times 10^4$, m/s	$D \times 10^9$, m ² /s	Ha'	E_{exp}	E_{calc}
25	3.70	2.49	0.802	1.08	1.25
40	4.24	3.44	0.967	1.19	1.36
55	5.26	4.52	1.02	1.24	1.40
70	6.18	5.70	1.10	1.89	1.45

Taking in consideration normal experimental errors in the measurements, physical constants, and the assumption $Sh = 2$ to be valid for the average particle diameter, the calculated enhancement factors correspond reasonably well with the measured factors although the particle size is not small enough in comparison to the diffusion layer thickness to assume homogeneous conversion (in fact $\delta \approx (1.1 - 1.3) d_p$). No condition of completely converted particles near the interface can be observed during these experiments.

Fig. 7. E vs. $1/d_p$ in case of $Sh = 2$ for two k_1 -values: $\epsilon_S = 0.10$, $m = 0.08$, $m(H_{2,g} - H_{2,g,eq}) = 73.6$, $\Delta P_{max} = 3.61 \cdot 10^{-4}$ mole/m³ solid.

Fig. 8. Physical adsorption with linear adsorption isotherm. E vs. adsorption capacity for different Ha' . $m = 0.5$, $\bar{A} = 0$, $\bar{P} = 0$, $A_g = 10$ mole/m³, $w_o = 10$ kg/m³.

GAS ABSORPTION IN SLURRIES OF ADSORBING PARTICLES

Mass transfer followed by heterogeneous reaction with insoluble particles, where the reaction with the particles in the liquid film plays an important role in describing the absorption flux, is relatively rare. A similar situation arises, however with absorption of gases like H_2S , SO_2 and hydrocarbons in aqueous slurries of activated carbon absorbing these gases (Alper, 1980; Nijjama, 1976; Kars, 1979; Kralj, 1984).

Specially the situation is similar if adsorption is very rapid and only takes place at the outside of the particle. Such an adsorption can be an accompanying process with a slow chemical reaction in the bulk of the slurry (Beenackers, 1985). An increase of the apparent value $k_1 a$ compared to $k_1 a$ of a system without activated carbon is observed, when a low concentration of particles smaller than the film thickness δ are added to the solution (Alper, 1980; Kralj, 1984). (Kars, 1979) even observed that particles with a diameter considerably greater than δ , can enhance the absorption rate.

For small adsorbing particles the film theory has been applied. According to this film theory the enhancement factor is then a unique function of the Ha -number (Jamakiraman, 1985; Nagy, 1984; Pal, 1982), but this theory can only be used if the adsorption capacity is large compared to the flux to the particles during the contact time. As will be demonstrated below this will not always be true, especially not when the adsorption capacity is low. This can be due to a low carbon concentration or a small adsorption equilibrium constant. However by using a similar model as described before we can take the limited adsorption capacity effect into account.

If a linear adsorption isotherm can be assumed:

$$A_S = \frac{P}{K_{ads}} \quad (14)$$

the maximum adsorption capacity will be:

$$P_{max} = m A_g K_{ads} \quad (15)$$

In contrast to the hydrides, where at reaching complete loading the conversion rate abruptly stops, here the flux to the particles decreases gradually because the driving force of the liquid to particle flux decreases as a result of a continuous increase of A_S during adsorption. Because the adsorption flux will already significantly decrease at relatively low loading of the particles, also the absorption rate immediately falls back.

The reduction of the enhancement factor as a consequence of the load on the adsorbing solids is shown in Fig. 8. Specially for high Ha' -numbers and low adsorption capacities ($\Delta P_{max} \epsilon_S / (1 - \epsilon_S)$) the enhancement factor E will be considerably reduced in comparison to the high adsorption capacity case. For low Ha' -numbers small adsorption capacities are sufficient to neglect the influence on the enhancement factor.

CONCLUSIONS

The penetration model assuming a pseudo-homogeneous system allows a description of mass transfer to a slurry with reacting or adsorbing particles. The finite capacity of the particles can be taken into account. Although the numerical model can easily accommodate other conversion or kinetic regimes attention is focussed on the fastest regime: mass transfer limitation to the particles.

Both in the case of a hydrogen/hydride type isotherm and of a linear adsorption isotherm, saturation of particles can considerably decrease the calculated enhancement factors. A critical Hatta number can be derived for this effect in case of the hydride slurries.

For conditions achieved in practice with hydride slurries only moderate enhancement factors are obtained.

The same holds for adsorption with linear isotherms but here the limited capacity of the particles immediately plays a role.

The pseudo-homogeneous theory can only be used if the particles are considerably smaller than the thickness of the penetration zone under conditions of reaction/adsorption.

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SYMBOL LIST

A	concentration of A in the liquid phase	mole/m ³ liquid
A _S	concentration of A in the liquid at equilibrium with the solid surface concentration	mole/m ³ liquid
a _s	specific interface of particles in liquid	m ² /m ³ liquid
D _A	diffusion coefficient of A in the liquid	m ² /s
a	dimensionless concentration of A: A/m.A _g	-
d _p	average particle diameter	m
e	dimensionless concentration A _S : A _S /m.A _g	-
E	enhancement factor defined by eq. (4)	-
Ha'	modified Hatta-number defined by eq. (5)	-
H _{2,g} eq	concentration of hydrogen in gas phase in equilibrium with dry hydride	mole/m ³ gas.
K _{ads}	adsorption equilibrium constant, eq. (14)	m ³ liq/m ³ solid.
k _l	liquid side of g/l interface mass transfer rate coefficient	m/s
k _{ls}	liquid to particle mass transfer rate coefficient	m/s
M	k _{ls} a _s τ	-
m	gas liquid distribution coefficient: C _l /C _g	-
Me	metal hydride concentration	mole/m ³ solid
P	concentration of product formed on solid surface	mole/m ³ solid
p	dimensionless concentration of P: P/Me	-
ΔP _{max}	maximum concentration difference: P _{max} - F	mole/m ³ solid
R	Me/m.A _g .ε _S /(1-ε _S)	-
Sh	Sherwood-number: k _{ls} d _p /D _A	-

t	time	s
w _c	concentration activated carbon	kg/m ³ slurry
x	distance from the gas liquid interface	m
z	$2x/\sqrt{(\pi\tau D_A)}$	-

Greek symbols

δ	film thickness in terms of film theory: D/k_1	m
τ	contact time according to the Higbie model: $4D^2/\pi.k_1^2$	s
θ	dimensionless contact time: t/τ	-
ϵ_s	volume fraction of solids in slurry	m ³ solid/m ³ slurry

Indices

c	complete conversion or critical
eq	equilibrium
g or G	gas phase
l	liquid phase
o	at the interface
∞	at infinite depth in the liquid
max	maximum
$\bar{i}$	bulk value of i