THE INFLUENCE OF ADSORPTION CAPACITY ON ENHANCED GAS ABSORPTION IN ACTIVATED CARBON SLURRIES

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Abstract—The enhanced absorption of gases in aqueous activated carbon slurries of fine particles is studied with a non-steady-state absorption model, taking into account the finite adsorption capacity of the carbon particles. It has been found that, for the different gas/activated carbon slurry systems studied in the literature, a remarkable similarity exists in the maximum achievable enhancement factor and the minimum solids concentration needed to reach the maximum enhancement. The enhanced physical absorption of gases via adsorption on the carbon particles, extensively investigated by Alper, is simulated with a penetration-type model. For the O₂ and CO₂ absorption it is demonstrated that, at the experimental bulk solids concentrations, no enhanced absorption could occur, because the adsorption capacities of these gases on activated carbon is too small. At these low solids concentrations, the enhancement is limited due to a rapid build-up of a layer of saturated particles close to the interface. High interfacial particle concentrations are necessary for any enhancement. It is therefore proposed, also on the basis of the observations in the literature, that the interfacial carbon concentration is much higher than the bulk concentration of the activated carbon particles. It is demonstrated that the non-steady-state absorption model can also be used for modelling enhanced gas absorption (adsorption followed by surface reaction). The absorption of O₂ in aqueous Na₂S activated carbon slurries is taken as an example.

INTRODUCTION

Slurry reactors where the solids either take part in the reaction or act as a catalyst are frequently used in industry. The solids can contribute as a reactant in two ways. They may present a source of soluble reactant that reacts in the liquid with the adsorbed gas, e.g. CO₂/SO₂ absorption into aqueous Ca(OH)₂ or Mg(OH)₂ slurries (Sada et al., 1984b; Alper and Deckwer, 1983) or the reaction can take place in the solid itself, e.g. H₂ absorption in metal hydride slurries (Beenackers and van Swaaij, 1982; Ptasinski et al., 1985).

In catalytic applications small particles may enhance the gas a absorption by catalysing the reaction in the diffusion film at the gas-liquid interface (Alper et al., 1980; Alper and Deckwer, 1983). In this case the particles should be small enough to be accommodated into the boundary layer. Alper and Deckwer (1983) have given an extensive review of this subject and roughly classified two categories of catalytic particles, namely particles which affect the liquid-side mass transfer coefficient due to their large adsorption capacity for the adsorbed gas, e.g. finely powdered activated carbon (Alper et al., 1980), and particles which enhance the reaction in the film by heterogeneous catalysis, e.g. Pt, Pd or immobilized enzymes on fine activated carbon particles (Alper et al., 1980; Wimmers et al., 1984; Wimmers, 1987).

The authors recently proposed a pseudo-homogeneous non-steady-state penetration model, which describes the mass transfer of a gas in a slurry containing particles with limited capacity for adsorption or reaction (Holstvoogd et al., 1986). It was demonstrated that the partial conversion/saturation of the activated carbon particles within the mass transfer zone strongly influences the enhancement factor. The purpose of the present study is to evaluate, using this penetration model, first the physical absorption of gases (O₂, CO₂ and propane) into aqueous activated carbon slurries (Alper's first category) and, second, the combined action of adsorption and reaction in slurry systems. The absorption of oxygen in aqueous Na₂S solutions with activated carbon is taken as an example of the second category.

LITERATURE

It has been generally observed that the absorption rate, when enhanced by fine activated carbon particles, increases with increasing activated carbon concentration until a certain concentration, after which the rate remains constant. Moreover studying many different gas/activated carbon slurry systems on the enhanced absorption, it is remarkable that the maximum enhancement is nearly always reached at the same activated carbon concentration level, this in spite of the large differences in reaction rate constants, which are to be expected. In Table 1 the minimum carbon concentrations necessary for reaching the limiting enhancement (mₐₑ) are summarized for several systems studied experimentally. The range of values

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Table 1. Minimum activated carbon (AC) concentration for maximum enhancement, \( m_{E=\infty} \), of gas absorption in various gas/AC slurry systems

<table>
<thead>
<tr>
<th>Gas-slurry system</th>
<th>( m_{E=\infty} ) (kg/m(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ( \text{O}_2 ) in aqueous AC slurry</td>
<td>1.0</td>
</tr>
<tr>
<td>(Alper et al., 1980): ( d_p &lt; 5 \mu m, T = 50^\circ\text{C} )</td>
<td></td>
</tr>
<tr>
<td>2. ( \text{CO}_2 ) in aqueous AC slurry</td>
<td>2.0-3.0</td>
</tr>
<tr>
<td>(Alper et al., 1980): ( d_p &lt; 5 \mu m, T = 25^\circ\text{C} )</td>
<td></td>
</tr>
<tr>
<td>3. Propane in aqueous AC slurry</td>
<td>No ( m_{E=\infty} ) known, but if ( m = 4.9 ), ( E = 1.2 )</td>
</tr>
<tr>
<td>(Kars et al., 1979): ( d_p \approx 34 \mu m )</td>
<td></td>
</tr>
<tr>
<td>4. ( \text{CO}_2 ) in aqueous Na(_2\text{CO}_3) buffer/AC slurry</td>
<td>2.0-3.0</td>
</tr>
<tr>
<td>(Alper et al., 1980): ( d_p &lt; 5 \mu m )</td>
<td></td>
</tr>
<tr>
<td>5. ( \text{O}_2 ) in aqueous Na(_2\text{SO}_4)/AC slurry</td>
<td>At 5°C: 1.5</td>
</tr>
<tr>
<td>(Alper and Deckwer, 1983; Alper and Ozturk, 1986b): ( d_p &lt; 5 \mu m )</td>
<td>At 25°C: 1.0</td>
</tr>
<tr>
<td>6. ( \text{O}_2 ) in aqueous Na(_2\text{S})/AC slurry</td>
<td>0.6-16</td>
</tr>
<tr>
<td>(Pal et al., 1982): ( d_p &lt; 5 \mu m, T = 80-150^\circ\text{C} )</td>
<td>~ 1.0</td>
</tr>
<tr>
<td>(Alper and Ozturk, 1986a): ( d_p &lt; 10 \mu m, T = 15, 25, 35^\circ\text{C} )</td>
<td>1.0</td>
</tr>
<tr>
<td>(Chandrasekaran and Sharma, 1977): ( d_p &lt; 100 \mu m, T = 70^\circ\text{C} )</td>
<td></td>
</tr>
<tr>
<td>7. ( \text{O}_2 ) in aqueous glucose/Pt on AC slurry</td>
<td>0.4</td>
</tr>
<tr>
<td>(Lee and Tsao, 1972): according to Alper no enhancement could be possible</td>
<td>10</td>
</tr>
<tr>
<td>(Alper et al., 1980): ( d_p &lt; 5 \mu m )</td>
<td></td>
</tr>
<tr>
<td>8. ( \text{CO}_2 ) in aqueous Na(_2\text{SO}_3) buffer/Pt or immobilized enzyme on AC slurry (Alper et al., 1980; Alper and Deckwer, 1983; Alper and Ozturk, 1986b; Sada and Kumazawa, 1982): ( d_p &lt; 20 \mu m )</td>
<td>2-3</td>
</tr>
</tbody>
</table>

for \( m_{E=\infty} \) is quite narrow in spite of the large differences in the investigated systems with only the data of Pal et al. (1982) [criticized by Alper and Ozturk (1986a)] forming an exception.

Usually, the limiting enhancement is explained (Alper and Deckwer, 1981; Sada and Kumazawa, 1982) as a consequence of reaching the minimum effective film thickness, \((d_{f,\text{eff}})_{\text{min}} = \delta_1/E_{\infty} = d_p\), which approaches the particle diameter, as illustrated in Fig. 1. A smaller effective film thickness cannot be reached, since in a layer of thickness approximating the particle diameter no particles are assumed to be present, meaning that no heterogeneous reaction can take place. However, from this model it cannot be easily understood why, for different physical and chemical systems, the maximum enhancement \((E^{\infty})\) should be reached at approximately the same \( m_{E=\infty} \) value.

**PHYSICAL ABSORPTION OF GAS IN AQUEOUS ACTIVATED CARBON SLURRIES**

### O\(_2\) absorption

Alper et al. (1980) have studied the absorption of \( \text{O}_2 \) in aqueous activated carbon slurries. In a stirred cell with flat gas–liquid interface the absorption rate, \( k_a \), has been measured as a function of the stirrer speed and the carbon concentration. In the absence of exact data, normal stirred-cell dimensions (where the liquid height is roughly equal to the cell diameter) have been assumed, resulting in an estimated specified interfacial area. In Table 2, for a stirrer speed of 250 rpm, the enhancement factor is presented as a function of the carbon concentration. Alper could only qualitatively explain the enhancement caused by the presence of carbon particles by postulating that the particles adsorb the gas in the film and transport it to the bulk of the liquid, the so-called “shuttle” or “grazing” mechanism (Alper and Deckwer, 1983; Kars et al.).

### Table 2. Data on \( \text{O}_2 \) absorption in activated carbon slurries estimated from Alper's experiments (Alper et al., 1980)

<table>
<thead>
<tr>
<th>( m_s ) (kg/m(^3))</th>
<th>( E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(&lt; 0.1 )</td>
<td>1.00</td>
</tr>
<tr>
<td>0.1</td>
<td>1.46</td>
</tr>
<tr>
<td>( \geq 1.0 )</td>
<td>3.38</td>
</tr>
</tbody>
</table>

\( T = 50^\circ\text{C}, D_{O_2} = 4.3 \times 10^{-9} \text{ m}^2/\text{s}, m = 0.012, d_p = 5 \mu m, \nu = 3 \times 10^{-4} \text{ m}^3/\text{s}. \) \( E = k_1 (\text{with AC})/k_1 (\text{without AC}). \)
The influence of adsorption capacity on enhanced gas absorption in activated carbon slurries. It is possible to simulate this process with the aid of the penetration model, which was developed earlier, taking into account the limited adsorption capacity of the activated carbon particles (Holstvoogd et al., 1986). In this model the gas phase component is considered to penetrate into the slurry by non-steady-state diffusion, whilst as a first approximation, mass transfer and chemical reaction and/or physical adsorption are treated as pseudo-homogeneous phenomena in the mass transfer film. A more exact solution involves an accurate description of the geometrical factors in the mass transfer zone (Holstvoogd, 1988), but is rather complicated and not necessary to demonstrate the effect of the finite adsorption capacity of the particles.

The absorption of $O_2$ in the liquid followed by adsorption on the carbon particle is treated as follows. Since the system $O_2$/activated carbon/water has an almost linear adsorption isotherm, the concentration of $A$ in the liquid, which is in equilibrium with the current amount of adsorbed gas on the particle, is

$$C_{A,e} = \frac{n_A}{m_s K_{ads}}.$$  \hspace{1cm} (1)

If, as a simplification of a much more complex process, the mass transfer to the particles and the adsorption on the particles are considered to be processes in series, the flow to the particles can be represented by

$$J_a = k_s a_s (C_A - C_{A,e}) = k_{ads} a_s (C_{A,s} - C_{A,e})$$  \hspace{1cm} (2)

where $C_{A,s}$ is the concentration of $A$ in the liquid at the liquid–solid interface. After defining $k_p$ as the overall particle rate constant for mass transfer to the particle with or without adsorption on the particle:

$$\frac{1}{k_p} = \frac{1}{k_s} + \frac{1}{k_{ads}}$$  \hspace{1cm} (3)

the total flux to the particles becomes

$$J_a = k_p a_s (C_A - C_{A,e}).$$  \hspace{1cm} (4)

Now assuming that a stagnant slurry package with a zero initial adsorbed gas loading (to start with a higher loading is also possible) stays for a contact time $\tau$ at the gas–liquid interface, and that no corrections for the effective diffusion coefficient have to be made, the basic equations of the penetration model are:

**mass balance of $O_2$:**

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} - k_p a_s (C_A - C_{A,e})$$  \hspace{1cm} (5)

**mass balance of adsorbed $O_2$:**

$$\frac{\partial n_A}{\partial t} = k_p a_s (C_A - C_{A,e})$$  \hspace{1cm} (6)

**boundary conditions:**

$$\begin{align*}
  & t = 0, x \geq 0 \quad \Rightarrow \quad C_A = C_{A,s} = n_A = 0 \\
  & t \neq 0, x = \infty \quad \Rightarrow \quad C_A = m C_{A,g} \\
  & x = 0, t \geq 0: \quad C_A = m C_{A,g}. \hspace{1cm} (7)
\end{align*}$$

The enhancement factor $E$ is defined as the average flux of $A$ with active particles divided by the average flux of $A$ with inert particles:

$$E = \frac{1}{\tau} \int_0^\infty -D_A \left( \frac{\partial C_A}{\partial x} \right)_{x=0} \, dt \left[ 2 \sqrt{\frac{D_A}{\pi \tau}} (C_{A,x=0} - C_{A,x=\infty}) \right]$$  \hspace{1cm} (8)

where $\tau$ is the Higbie contact time of the stagnant element with the gas phase:

$$\tau = \frac{4 D_A}{\pi k_p^2}.$$  \hspace{1cm} (9)

A Hatta number is defined for heterogeneous applications:

$$Ha_h = \sqrt{k_p a_s D_A / k_i}$$  \hspace{1cm} (10)

where

$$a_s = \frac{6 m_s}{\rho_p d_p}.$$  \hspace{1cm} (11)

Although the saturation of the particles will take place more gradually, an equivalent layer of slurry in which the particles are completely saturated may be calculated:

the mean flux to the particle is

$$J_{ad} = J_{enh} - J_{phys} = (E - 1) k_m C_{A,g}$$  \hspace{1cm} (12)

equivalent converted layer thickness:

$$\delta_{sl} = \frac{J_{ad} \tau}{n_A,\max}.$$  \hspace{1cm} (13)

This set of parabolic differential equations [eqs (5–7)] has been solved numerically [see Appendix A (Holstvoogd et al., 1986)]. The model assumes that the slurry package at the interface is stagnant, which means that the particles stay motionless during the contact penetration time. This is justifiable giving that particle movement can only be caused by Brownian movement, which only becomes significant for particles which are two orders of magnitude smaller than the activated particles mentioned here.

Most model parameters can be easily estimated; the more difficult parameters are the adsorption equilibrium constant ($K_{ads}$) and the adsorption rate constant ($k_{ads}$). For the system $O_2$/activated carbon/$H_2O$, $K_{ads}$ has been estimated by extrapolating the $K_{ads}$ measurements of Recasens et al. (1984) at 10, 15 and 20°C, to 50°C (the temperature of Alper's absorption experiments) which results in $K_{ads} = 7.6 \times 10^{-3}$ m$^3$/kg. Calculation of $K_{ads}$ from the data of Li and Deckwer (1982) results in an even smaller value: $K_{ads}$ (30°C) = $4.5 \times 10^{-3}$ m$^3$/kg. Recasens has measured the adsorption rate per unit of particle density at 50°C as $k_a = 2.8 \times 10^{-3}$ m$^3$/kg s. The adsorption rate of a particle then becomes $k_{ads} = k_a \times \rho_p \times d_p / 6 = 1.2 \times 10^{-6}$ m/s (assuming a dry particle density of 850 kg/m$^3$ and a mean particle diameter of 3 μm). The
liquid-to-particle mass transfer coefficient can be calculated by assuming $Sh = 2$ to be valid for the average particle diameter, resulting in $k_p = 2.9 \times 10^{-3} \text{ m/s (} d_p = 3 \mu\text{m})$. The simulations reported here, have been performed on the basis of $K_{ads} = 7.6 \times 10^{-3}$ and a $k_p$ value varying between $1.2 \times 10^{-6}$ for adsorption limitation and $2.9 \times 10^{-3}$ for mass transfer limitation to the particle.

In a few of the simulations with the present adsorption model, the influence of adsorption capacity, and adsorption rate on the enhancement factor have also been investigated. For a typical situation the enhancement factor was calculated as a function of the overall particle rate constant ($k_p$) for different solids concentrations. Figure 2(a) shows that the equivalent saturated film thickness ($\delta_{sl}$), or fraction saturated particles in the hydrodynamic film, increases with $k_p$, but reaches an almost asymptotic value as soon as the diffusion flux is insufficiently large for significant additional growth. When, during a comparatively short part of the contact time a relatively thick layer of saturated particles has been formed, the enhancement factor becomes almost constant [Fig. 2(b)]. It is obvious that high solid concentrations lead to smaller $\delta_{sl}$ and larger enhancement factors.

In order to evaluate the effect of a saturated layer on the enhancement factor it is necessary to derive, by substituting $n_{max}$ and $J_{ads}$ in eq. (13), that the minimum ratio between $\delta_{sl}$ and the hydrodynamic film thickness:

$$\frac{\delta_{sl}}{\delta_t} = \frac{4(E - 1)}{\pi m_s K_{ads}}.$$

The simulations show that for saturation levels of less than a few percent, there is no decrease in $E$ (line 1 of Fig. 3). In this case the enhancement is a unique function of $Ha_h$, which is independent on $m_s$ and not on $K_{ads}$, and given by the well-known penetration theory solution with constant reaction rate:

$$E = Ha_h \tanh (Ha_h).$$

Taking a 5% saturation level as the maximum level for the absence of saturation conditions, a minimum adsorption capacity can be derived:

$$m_s K_{ads} > \frac{Ha_h}{\tanh (Ha_h)} - 1.4 \frac{0.05}{\pi}.$$  

With this relation the adsorption capacities that are necessary to avoid saturation can now be determined, for instance

$$\text{if } Ha_h = 2.0 \text{ then } K_{ads} m_s > 27.4.$$

A transition region occurs when the relative saturation layer is not greater than 10–30%, demonstrated by line 2 in Fig. 3. Then the adsorption capacity as well as $Ha_h$ determine the enhancement factor. For saturation levels over 40%, the enhancement factor becomes

$$E^2 = \frac{k_p}{m_s} \left( \frac{Ha_h}{\tanh (Ha_h)} - 1.4 \right) \frac{0.05}{\pi}.$$
The influence of adsorption capacity on enhanced gas absorption in activated carbon slurries

The enhancement factor as a unique function of the adsorption capacity.

\[ E = \sqrt{1 + m_i K_{ads}}. \]  

This effect is due to a large saturated layer being built up during a comparatively small fraction of the contact time of the slurry package meaning that, after this period, the mass transfer into the package is limited by the diffusion through the saturated layer. Thus only during the first fraction of the contact time can enhanced absorption take place and so the magnitude of the adsorption rate ceases to be important. A large absorption rate constant increases the absorption rate in the period of non-saturation, but also leads to the saturated layer being formed sooner, resulting in practically the same enhancement as with a smaller adsorption rate constant.

In order to investigate what levels of film solids concentrations are required in order to reach the experimental \( E \) values obtained by Alper et al. (1980) in their experiments concerning \( \text{O}_2 \) absorption in activated carbon slurry (see Table 2), the enhancement factors are calculated and plotted against the solids concentration in Fig. 5 for the two extreme \( k_p \) values. If \( k_p \) is determined by the adsorption rate, line 3 represents the simulations: here capacity and \( H_{ads} \) determine the enhancement. The influence of capacity can be observed by a comparison with line 2, where saturation is excluded. At the high \( k_p \) value, \( k_p = k_i \) (see line 1), the relationship between \( E \) and the solids concentration is independent of \( H_{ads} \) [eq. (18)].

Alper measured for an average bulk concentration of 0.1 kg/m³, an enhancement factor of 1.46. In our simulations this enhancement could only be reached at solids concentrations of 240 and 140 kg/m³ for \( k_p = k_{ads} \) and \( k_p = k_i \), respectively, and with \( K_{ads} = 7.6 \times 10^{-3} \text{ m}^3/\text{kg} \). These concentrations are far higher than the actual bulk concentrations. Experimentally the limiting enhancement factor, \( E^\infty \) (=3.38), is reached at bulk loadings of higher than 1.0 kg/m³: however, the simulations have demonstrated that very high carbon concentrations (> 500 kg/m³) are needed to calculate such an enhancement. On the other hand, the adsorption capacities needed to avoid any saturation can be estimated with eq. (16). For an enhancement factor of 1.46 an adsorption capacity, \( K_{ads} \) larger than 11.7 is needed and unrealistically high solids concentrations (> 1500 kg/m³) would be necessary to reach this capacity with even higher concentrations being needed for the limiting enhancement factor.

Given that the simulations clearly show that, for the experiments conducted by Alper, the saturation effect had a considerable influence on the \( \text{O}_2 \) absorption, and that the carbon concentration in the boundary layer at the gas-liquid interface should have been much larger than the bulk concentration, the limiting value of \( E \) in Alper’s experiments was probably caused by a maximum solids concentration at the interface rather than by a solids-free zone at the interface. Saturation was not taken into account by Alper et al. since, in the stationary film model used by them, it cannot be incorporated in a meaningful way.

**CO₂ absorption**

Physical absorption enhancement of \( \text{CO}_2 \) in water by activated carbon particles has been studied by Alper et al. (1980). A maximum absorption enhancement of about 4 has been observed at bulk solids concentrations higher than 2–3 kg/m³.

Before the effect of saturation on \( E \) can be simulated, several physical parameters have to be known. The adsorption equilibrium constant has been estimated by linearizing the experimental adsorption isotherm measured by Li and Deckwer (1982). In the absence of actual data the liquid-side mass transfer coefficient was found by dividing the measured \( k_d \) without particles by the estimated specific contact area [assuming that the referred stirred cell 2 is the same or similar to the cell used later by Alper and Ozturk (1986a)]. The adsorption rate constant is not known, and therefore \( k_p \) was varied over several orders of magnitude, with \( k_p \approx k_i \) as the maximum value. All the kinetic and system parameters used for the simulations are summarized in Table 3.
Table 3. Kinetic and system parameters for simulations of CO₂ absorption in carbon slurries (Alper et al., 1980)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>T = 25°C</td>
<td></td>
</tr>
<tr>
<td>a₀ = 20 m²/m³</td>
<td></td>
</tr>
<tr>
<td>k₁ = 2.5 × 10⁻⁵ m/s</td>
<td></td>
</tr>
<tr>
<td>m = 0.40</td>
<td></td>
</tr>
<tr>
<td>K_ads = 3.3 × 10⁻₇ m³/kg</td>
<td></td>
</tr>
<tr>
<td>ρₑ = 850 kg/m³</td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Kinetic and system parameters for simulations of propane adsorption in carbon slurries (Kars et al., 1979)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>T = 25°C</td>
<td></td>
</tr>
<tr>
<td>m = 3.69 × 10⁻²</td>
<td></td>
</tr>
<tr>
<td>k₁ = 3.9 × 10⁻⁴ m/s</td>
<td></td>
</tr>
<tr>
<td>D = 1.2 × 10⁻⁶ m²/s</td>
<td></td>
</tr>
<tr>
<td>ρₑ = 850 kg/m³</td>
<td></td>
</tr>
<tr>
<td>Experimental value for mₛ = 4.94 kg/m³ is E ≈ 1.32</td>
<td></td>
</tr>
</tbody>
</table>

In the preceding section the required adsorption capacity for the condition E = Hₛ mₛ = 2, was derived as K_ads mₛ > 27.4 [eq. (17)]. Experimentally, the minimum solids concentration necessary to reach the maximum enhancement, Eᵐ, was found to be 3 kg/m³, leading to an adsorption capacity of 9.9 × 10⁻², which is far to small to avoid saturation conditions. Assuming that no saturation would occur, an adsorption rate constant of 0.1 × 10⁻⁵ m/s would be large enough to yield an enhancement factor of 4 at mₛ = 3 kg/m³; however, neglecting saturation is not realistic. For three different adsorption rate constants, k_ads = 10⁻⁶, 10⁻⁴ and 10⁻² m/s, the enhancement factor is calculated as a function of the solids concentration with the same numerical model as used for O₂ adsorption. In Fig. 6 the relationships between E and mₛ are plotted for each overall adsorption rate constant. At large adsorption rates E is completely determined by the adsorption capacity (line 1), but is only a function of Hₑ mₛ at the smallest adsorption rate. The minimum required solids concentration to reach Eᵐ can be estimated from line 1 in Fig. 6, resulting in concentrations as high as 450 kg/m³. Clearly, the interfacial solids concentration has to be far higher than the bulk concentration.

Propane absorption

Kars et al. (1979) has found, for one particular case, that large activated carbon particles of 34 μm can enhance the propane absorption rate in water (Table 4).

In this case the adsorption capacity, K_ads mₛ (= 1.97 m³/kg × 4.94 kg/m³), is 9.7. The required capacity to reach the experimental enhancement factor of 1.32 is determined to be 8.1, so saturation of the particles has not occurred. However, high solids concentrations in combination with high adsorption rates are necessary to calculate this enhancement factor. The film model cannot calculate any enhancement, since in this case the stationary film thickness is 10 times smaller than the particle diameter. However considering a penetration model, enhancement could be calculated provided the concentration of carbon particles is high, since for longer contact times the penetration depth is large enough for absorbed gas to react at the particle surface. The enhancement is probably caused by particles, preferentially attracted to the gas-liquid interface, increasing the boundary concentration.

It should be realized that in Kars' system, the pseudo-homogeneity conditions are seriously violated and therefore enhancement can only be accurately modelled with a non-steady-state heterogeneous absorption model.

O₂ ABSORPTION IN AQUEOUS Na₂S SOLUTIONS WITH ACTIVATED CARBON PARTICLES

Literature discussion

In this section a paper of Alper (Alper and Ozturk, 1986a) on enhanced O₂ absorption in aqueous Na₂S solutions by activated carbon particles will be evaluated. Chandrasekar and Sharma (1977) and Pal et al. (1982) have already investigated this system at temperatures above 70°C. Lefers et al. (1978) and later Sada et al. (1984a), who interpreted both his own and Lefers' measurements in terms of a Langmuir–Hinshelwood mechanism, studied the O₂ absorption rate at about room temperature. Lefers found the following reaction equation:

\[ r_O = k_0 C_{O_2}^{0.75} C_S^{0.42} \text{ (mol/s–g catalyst)} \] (19)
while Sada proposed that
\[
    r_o = k_0 \frac{C_{O_2} C_S}{[1 + (K_{O_2} C_{O_2})^{0.5} + (K_S C_S)^{1.5}]^{3/2}} \quad \text{(mol/(s-g catalyst))}. \quad (20)
\]

Both Sada and Lefers used very low carbon concentrations of about 0.05 kg/m³, and it can therefore be understood that they never reached the enhanced absorption regime. However, Alper and Ozturk (1986a) have measured enhancement of O₂ adsorption in sulphide oxidation at 15, 25 and 35°C with carbon loadings up to 4 kg/m³. Alper found that the adsorption flux rapidly increases with increasing carbon concentration to its maximum value at carbon concentrations of about 1 kg/m³. This is the same picture as has been observed with the physical absorption cases, discussed above.

An interesting aspect in the experimental results of Alper is that, at constant O₂ interface concentration, the maximum enhancement factor \( E^\infty \) substantially increases with increasing bulk concentration of sulphide \( (C_S) \) (see Table 5). Alper proposed as a possible explanation of the independence of the absorption rate above a certain activated carbon concentration, that a particle-free liquid zone of thickness \( \lambda \) adjacent to the interface exists and, if the reaction rate is increased sufficiently by increasing the carbon loading or reactant that the unreacted dissolved gas may be effectively confined to this thin particle-free layer. However, this model fails to give an explanation for the experimental fact that \( E^\infty \) increases with the sulphide concentration (see Fig. 2 of Alper and Ozturk (1986a)), because as elucidated in Fig. 7 the maximum O₂ gradient at the interface is already reached at the lowest sulphide concentration; the reaction plane cannot come any nearer to the interface and therefore no further increase of \( E \) could be possible.

In the preceding section it was determined that the high physical absorption rates of O₂ and CO₂ in activated carbon slurries must be a consequence of increased carbon concentrations at the interface and this phenomena can clarify the dependence of \( E^\infty \) on the sulphide concentration. In the absence of the layer \( \lambda \), the reaction can progress nearer to the interface, where the reaction rate is increased by higher sulphide concentrations resulting in the larger O₂ concentration gradients and larger maximum enhancement factors.

Taking this plausible explanation for the sulphide dependence of \( E^\infty \), and the similarity of the behaviour of \( E \) with activated carbon concentration from this system with that of the physical absorption cases, it is suggested that, here also, the carbon particle concentration at the gas–liquid interface is higher than in the bulk of the slurry up to a limiting value.

**Simulations**

Attempts were made using a Langmuir–Hinschelwood mechanism for describing the reaction rate at the activated carbon particle, but there were too many uncertainties in establishing the adsorption equilibrium and kinetic rate constants (the calculated constants of Lefers and Sada were measured at much lower sulphide concentrations, somewhat higher temperatures, and different pH compared to those in Alper's experiments). The experimental results of Alper were therefore only simulated with a more simple reaction rate mechanism. Alper suggested that, since in the enhanced absorption regime the measured orders of O₂ and sulphide in the absorption rate were, respectively, about 0.75 and 0.5, the true reaction orders of O₂ and sulphide in the reaction rate equation should be 0.5 and 1, respectively. These values are used in the simulations, while the adsorption flux from the

<table>
<thead>
<tr>
<th>N = 120 rpm</th>
<th>( D_{O_2} = 3.4 \times 10^{-9} \text{ m}^2/\text{s} )</th>
<th>( d_p = 3 \mu\text{m} )</th>
<th>( C_S ) (mol/m³)</th>
<th>( E^\infty )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_l = 5.58 \times 10^{-5} \text{ m/s} )</td>
<td>( \rho_p = 550 \text{ kg/m}^3 )</td>
<td>62.5</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>( C_p = 43.3 \text{ mol/m}^3 )</td>
<td>( k_s = 2D_{O_2}/d_p = 1.6 \times 10^{-3} \text{ m/s} )</td>
<td>62.5</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>( m = 0.012 )</td>
<td>( \rho_S = 1 \text{ kg/m}^3 )</td>
<td>130</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>( \mu_{O_2} = 1.9 \times 10^{-3} \text{ m}^2/\text{kg} )</td>
<td>( pH = 13 )</td>
<td>250</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>( K_{O_2} = 10.9 \times 10^{-3} \text{ m}^2/\text{kg} ) (Nijama and Smith, 1977)</td>
<td>( K_S = 20.8 \times 10^{-3} \text{ m}^2/\text{kg} ) (Ramachandran and Smith, 1978)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
liquid to the particles is simplified as mass transfer to the particle followed by surface reaction in series. As will be shown, the influence of this mass transfer resistance is not very important. The flux to the particles becomes

$$J_a = k_0 a_s (C_{O_2} - C_{O_2,a}) = k_0 n_0 2.5 n_s$$

$$= k_0 (K_{o_2} m_s C_{O_2,a})^{0.5} (K_m c_{S, a})^{1.5}.$$  (21)

The mass balance of the adsorbing $O_2$ is

$$\frac{\partial C_{O_2}}{\partial t} = D \frac{\partial^2 C_{O_2}}{\partial x^2} - k_a a_s (C_{O_2} - C_{O_2,a})$$

with boundary conditions:

$$t = 0, x \geq 0 \text{ } C_{O_2} = C_{O_2,a} = 0$$

$$t \neq 0, x \to \infty \text{ } C_{O_2} = C_{O_2,a} = 0$$

$$x = 0, t \geq 0 \text{ } C_{O_2} = m C_g.$$  (23)

The decrease of the adsorbed sulphide concentration in the direction of the interface is negligible compared to the decrease in the oxygen concentration in the liquid, because the sulphide concentration is much larger, and also $K_S > K_{O_2}$ and the mass balance of sulphide is therefore omitted. The set of eqs (21)-(23) is solved in the same way as before and is detailed in Appendix B.

For the proposed kinetics the pseudo-first-order reaction rate constant becomes

$$k_{1p} = k_0 (K_s m_S c_{S,a})^{0.5}.$$  (24)

At the gas-liquid interface the $O_2$ concentration is known to be equal to $m C_g$. The pseudo-first-order reaction rate constant therefore has its minimum value at the interface, $k_{1p, min}$. Since the reaction is of the order 0.5 in oxygen, $k_{1p}$ is dependent on both the penetration time and the distance from the interface. In the model this non-linearity of $k_{1p}$ has been taken into account. The effects of the non-linearity are not very large, as can be seen in Fig. 8, where the exact results of the simulations are compared with those obtained with the constant minimum $k_{1p}$. The simulations have been performed using the data in Table 5, assuming $d_p \approx 3 \mu m$, and the bulk concentration of $O_2$ being zero. Assuming that the maximum carbon concentration at the interface is $150 \text{ kg/m}^3$, it was found that with a $k_0$ value of $5 \times 10^{-2}$ the calculated absorption fluxes match the experimental fluxes measured by Alper. Then the overall mass transfer rate to the particles is determined for 90% by the reaction rate and for 10% by the mass transfer rate to the particles.

In order to verify that the increasing local $k_{1p}$ value has no effect on the absorption rate orders of $O_2$ and sulphide, the calculated adsorption flux is shown as a function of the oxygen concentration and the sulphide concentration in Figs 9 and 10, respectively. At high carbon concentrations the orders are indeed almost in agreement with those found experimentally, since the
overall mass transfer rate to the particle is controlled by the surface reaction. However, at low carbon concentrations another dependence is observed, which is clearly demonstrated in Fig. 9 where the overall order of $O_2$ changes from about 0.75 at low $C_g$ to about 1 at high $C_g$. Here the adsorption moves from the enhanced absorption regime ($H_a < 2$) to the physical absorption regime ($H_a < 0.2$), because $k_{1p}$ and therefore also $H_a$ are inversely proportional to the adsorbed gas concentration.

**DISCUSSION AND CONCLUSIONS**

In the literature survey it was observed that, for many different systems, in which activated carbon particles are used as a catalyst, both the experimental values of the minimum activated carbon concentration required for maximum enhancement of gas absorption and the values of the maximum enhancement factors are of approximately equal size. This remarkable resemblance can be caused by the same physical effect: the activated carbon concentration in the diffusion film at the interface cannot increase anymore after reaching a limiting value.

The ability of the proposed model to calculate local adsorbed gas concentrations allowed the enhanced physical absorption of $O_2$, $CO_2$ and propane in activated carbon slurries to be simulated. The experimental enhancement factors can only be explained by assuming that, due to interfacial effects and surface properties of the carbon particles, the interfacial carbon concentration is much larger than the bulk concentration. These high concentrations are necessary since, otherwise, during the contact time of a slurry package at the gas-liquid interface, the activated carbon particles quickly become completely saturated with adsorbed gas and therefore unable to significantly enhance the absorption process.

Several authors have suggested that the interfacial activated carbon concentration could be larger than the bulk concentration. Lee and Tsao (1972) visually observed that there were carbon particles floating on the liquid surface, and concluded that this tendency causes a higher local concentration and thus accounts, through the higher local reaction rate, for the extra enhancement. Alper and Ozturk (1986a) agree with the suggestion of Sada and Kumazawa (1982), who evaluated experimental results of Alper (Alper et al., 1980; Alper and Deckwer, 1981) on glucose oxidation in Pt/activated carbon and the hydrolysis of $CO_2$ in the presence of immobilized carbonic anhydrase, that the catalyst particle concentration in the range of $A < x < D/k$, should be somewhat higher than in the bulk liquid phase. However they still adhered to the idea of a layer $A$, which does not contain any particles. This explanation for maximum enhancement is not very plausible. In fact, from the experiments of Alper and Ozturk (1986a), there is experimental evidence that the existence of this layer could not cause the maximum enhancement, since $E^\infty$ during $O_2$ absorption in $Na_2S$ solutions increases at higher bulk sulphide concentration. Within the framework of the particle-free layer model this cannot be the case, because $E^\infty$ is reached already at a lower sulphide concentration, and this is assumed to be caused by the diffusion limitation of oxygen. Another indication for a higher interfacial concentration is given by Wimmers et al. (1984). They measured enhanced absorption of gas into a stagnant liquid, in which catalytic activated carbon particles are attached on the bubble surface by their surface properties in a volume fraction of about 16%, corresponding to 140 kg/m$^3$ activated carbon ($\rho_p = 850$ kg/m$^3$). The authors' conclusions have been recently confirmed by Wimmers, (1987), who has shown that small Pd/activated carbon particles have a strong tendency to be attracted to the gas-liquid surface. He demonstrated that the adhesion of the particles can be described by a Freundlich-type adsorption isotherm, in which the particle film concentration increases via a power function with the bulk particle concentration until a maximum film concentration is reached (for 10 wt % Pd/activated, carbon this is about 235 kg/m$^3$ or 0.12 vol %). Furthermore, he demonstrated that the enhancement factor for absorption followed by heterogeneous catalyzed reaction is strongly affected by the presence of dispersed bubbles in the liquid since this increases the contact between gas-liquid surface and solid catalyst particles.

It has been shown with the present model that, in the case of a strong saturation of particles at the interface, the enhancement factor becomes essentially independent of the heterogeneous Hatta number and will be a function of adsorption capacity alone. The maximum enhancement obtainable in a slurry is probably limited by the already proposed maximum interfacial concentration.

In conclusion the importance of more experimental work in the field of surface effects in heterogeneous system is stressed as the need for heterogeneous models in describing enhanced absorption, when high reaction rates are involved.

**NOTATION**

- $a$: specific gas-liquid contact area, m$^2$/m$^3$ liquid
- $a_s$: specific interface of solids in liquid, m$^2$/m$^3$ liquid
- $C$: concentration of gas component in the liquid phase, mol/m$^3$ liquid
- $C_{A,c}$: equilibrium concentration of gas component $A$ on the carbon particle, mol/m$^3$ liquid
- $d_p$: particle diameter, m
- $D$: diffusion coefficient in liquid or slurry, m$^2$/s
- $E$: enhancement factor [eq. (8)]
- $E^\infty$: maximum enhancement factor
- $J$: molar flux, mol/(m$^2$ s)
- $H_a$: modified Hatta number for heterogeneous applications [eq. (10)]
- $K$: adsorption equilibrium constant, m$^3$ liquid/kg solid
$K_{ads}$ adsorption equilibrium constant [eq. (1)], m$^3$ liquid/kg solid
$k_{ad}$ adsorption rate constant, m/s
$k_a$ adsorption rate constant per unit particle density, m$^3$/kg s
$k_l$ liquid-side mass transfer coefficient, m/s
$k_{o}$ reaction rate constant [eq. (21)], m$^{1.5}/$(mol$^{0.5}$/s)
$k_p$ overall particle adsorption rate constant [eq. (3)], m/s
$k_s$ liquid-to-solid mass transfer coefficient, m/s
$k_{1,p}$ pseudo-first-order reaction rate constant [eq. (24)]
$m$ gas solubility ($C_1/C_s$)
$m_s$ concentration of solids, kg solid/m$^3$ liquid
$m_{E}^{\infty}$ concentration of solids when $E^{\infty}$ is just reached, kg solid/m$^3$ liquid
$n$ adsorbed gas concentration, mol/m$^3$ liquid
$n_{max}$ maximum adsorbed gas concentration ($mC_0K_{ads}m_s$), mol/m$^3$ liquid
$r$ reaction rate at particle surface, mol/(s-g catalyst)
$t$ time, s
$x$ distance from gas–liquid interface, m
$z = 2x/(\sqrt{\pi}D_t)$

Greek letters
\[ \delta_a \] equivalent saturated film layer, m
\[ \delta_f \] film thickness in terms of film model ($D/k_c$), m
\[ \lambda \] particle-free liquid zone at gas–liquid interface, m
$\rho_p$ dry particle density, kg/m$^3$ solid
$\tau$ contact time [eq. (9)], s

Subscripts
$A$ component A
ad adsorption
g gas phase
l liquid phase
max maximum
min minimum
$O$ dissolved oxygen
$s$ at solid
$S$ sulphide

Superscript
– mean value

REFERENCES


APPENDIX A

In this appendix in a concise way the numerical treatment of differential eqs (5) and (6) with their boundary conditions (7) will be discussed.

Transformation into dimensionless form:

\[
\frac{\partial a}{\partial \theta}(\theta, z) = \frac{4 \partial a^2}{\partial z^2}(\theta, z) - M[a(\theta, z) - e(\theta, z)]
\]
(A1)

\[
\frac{\partial p}{\partial \theta}(\theta, z) = \frac{M}{R}[a(\theta, z) - e(\theta, z)]
\]
(A2)

boundary conditions:

\[
\begin{align*}
\theta = 0, & \quad z \geq 0 \quad \Rightarrow a = e = p = 0 \\
\theta \neq 0, \quad z \to \infty & \quad a = e = p = 0
\end{align*}
\]

\[
a(0, z) = \frac{\partial a}{\partial z}(0, z)
\]

if \( K_g = \frac{k_g}{m_{el}} \to \infty \) then \( a(\theta, 0) = 1 \)

with

\[
a = \frac{C_A}{m_{C_A}}, \quad p = \frac{n_{max}}{e}, \quad e = \frac{C_{Ae}}{m_{C_A}}, \quad \theta = \frac{t}{\tau}, \quad z = \frac{2x}{\partial \sqrt{\pi D\tau}}
\]

\[
M = k_p a \tau, \quad R = \frac{n_{max}}{C_{Ae}}
\]

Transformation of time and spatial parameters for better accuracy:

\[
z = \phi(y) \quad \text{with} \quad \phi(0) = 0, \quad \phi(1) = z_w, \quad \phi'(0) = 0
\]

\[
\theta = \psi(w) \quad \text{with} \quad \psi(0) = 0, \quad \psi'(0) = 1
\]

for instance \( \psi(w) = w^a \).

Incorporation of these transformations into differential eqs (A1) and (A2):

\[
\frac{1}{\psi(w)} \frac{\partial a(w, y)}{\partial w} = \frac{4}{\psi(w)} \frac{\partial a^2}{\partial y^2}(w, y) \left[ \frac{1}{\psi(w)} \frac{\partial a(w, y)}{\partial y} - M[a(w, y) - e(w, y)] \right]
\]

\[
\frac{1}{\psi(w)} \frac{\partial p(w, y)}{\partial w} = \frac{M}{R} \left[ a(w, y) - e(w, y) \right]
\]

boundary conditions:

\[
w = 0; \quad \forall y: \quad a = e = p = 0
\]

\[
y = 0; \quad \forall w: \quad K_g \phi'(0)[a(w, 0) - 1] = \frac{\partial a(w, 0)}{\partial y}
\]

\[
y = 1; \quad \forall w: \quad a = e = p = 0
\]

Discretization of the differential equations according to the Baker and Oliphant scheme with the following discretization formulas:

\[
y = ih, \quad h = 1/N \quad (N \text{ is total number of spatial steps})
\]

\[
w = (j+1)k, \quad k = 1/NW \quad (NW \text{ is total number of time steps})
\]

\[
\begin{align*}
\frac{\partial u^{i+1}}{\partial w} & = \frac{3u^{i+1} - 4u^i + u^{i-1}}{2k} \\
\frac{\partial^2 u^{i+1}}{\partial y^2} & = \frac{u^{i+1} - 2u^i + u^{i-1}}{h^2} \\
\frac{\partial y}{\partial y} \left[ f(y) \frac{\partial u^{i+1}}{\partial y} \right] & = (g(h) f((i-0.5)h) u^{i+1} + g(h) f((i+0.5)h) u^{i+1})/h^2
\end{align*}
\]

gives:

\[
\begin{align*}
\text{for } i = 1, 2, 3, \ldots, N-1: \quad & \text{after substituting}

p^{i+1} & = e^{i+1} = \frac{4e^i - e^{i-1} + \frac{2kM}{3} \psi'(j+k) a^{i+1}}{1 + \frac{2kM}{3R} \psi'(j+k)}
\end{align*}
\]

the discretized eq. (A3) becomes

\[
\begin{align*}
\psi'(w) & = \psi'(w - \psi(w)) = \left( \int \frac{\partial \phi}{\partial y} \left[ \frac{\phi((i-0.5)h) + \phi((i+0.5)h)}{2} \right] \right)
\end{align*}
\]

\[
\begin{align*}
\text{for } i = 0: \quad & \text{with}

a_0^{i+1} & = a_0^{i}, \quad e_0^{i+1} = e_0^{i}, \quad h \frac{\partial a_0^{i+1}}{\partial y} = \frac{2kM}{3R} \psi'(j+k)
\]

\[
\begin{align*}
\frac{\partial a^{i+1}}{\partial w} & = \frac{1}{2} \frac{\partial^2 a^{i+1}}{\partial y^2} + \ldots
\end{align*}
\]

with, at \( i = N-1, a_N = \psi_N = 0 \).

For every time step \( j \) the set of \( N \) equations \( 1 \times (A6) + (N-1) \times (A5) \) can be solved after transforming the \( N \times N \) matrix into a tridiagonal band matrix, which is possible because, apart from the three centre diagonals, the matrix is filled with
zeros. A Crout decomposition method is used to solve this transformed matrix. For more details, the reader is referred to Baker and Oliphant (1960), Cornelisse et al. (1980) and Versteeg (1986).

**APPENDIX I**

Here the numerical treatment of differential eq.(22) with its boundary conditions is discussed. The treatment is the same as followed in Appendix A: only the most important differences are shown.

Transformation into dimensionless form:

Equation (22) becomes

\[
\frac{\partial a}{\partial \theta}(\theta, z) = \frac{4}{\pi} \frac{\partial^2 a}{\partial z^2}(\theta, z) - M[a(\theta, z) - \epsilon(\theta, z)].
\]

Equation (21) leads to the following relation between \( e \) and \( a \):

\[
e = a + \frac{\beta}{2} - \sqrt{\left(\frac{\beta}{2}\right)^2 + \beta a} \]

with

\[
\beta = \left(\frac{k_0}{k_c a_s}\right)^2 (K_s m_s C_s) \frac{K \rho m}{m C_d}, \quad \alpha = \frac{C_{O_2}}{m C_d}, \quad \alpha = \frac{C_{O_2}}{m C_d}, \quad \theta = \frac{1}{\pi}, \quad M = k_c a_s \tau.
\]

Time and spatial transformation: see Appendix A.

After linearization by a Taylor expansion of the root term in the equation between \( e \) and \( a \):

\[
\sqrt{\left(\frac{\beta}{2}\right)^2 + \beta a} = \sqrt{\left(\frac{\beta}{2}\right)^2 + \frac{\beta a}{2} + \frac{\beta a}{2}}
\]

and substitution of \( e = a \) in the discretized equations, the relation between \( a_1^{i+1}, a_i^{i+1}, a_i^{i+1} \) and \( a_i, a_i^{i-1} \) becomes:

for \( i = 1, 2, 3, \ldots, N-1 \):

\[
\left\{ \begin{array}{l}
4 \\
\pi \phi'(i h) \phi'(i - 0.5 h) h^2 \\
\end{array} \right\} a_i^{i+1} + \left\{ \begin{array}{l}
-3 \\
2 k \phi'(i + 1) k \\
\end{array} \right\} a_i^{i+1} + \left\{ \begin{array}{l}
1 \\
\phi'(i - 0.5 h) \\
\end{array} \right\} a_i^{i+1} + \left\{ \begin{array}{l}
1 \\
\phi'(i + 0.5 h) \\
\end{array} \right\} a_i^{i+1} = \left\{ \begin{array}{l}
M \beta \\
2 \sqrt{\left(\frac{\beta}{2}\right)^2 + \beta a} \\
\end{array} \right\} a_i^{i+1} + \left\{ \begin{array}{l}
4 \\
\pi \phi'(i h) \phi'(i + 0.5 h) h^2 \\
\end{array} \right\} a_i^{i+1} + \left\{ \begin{array}{l}
-4 a_i + a_i^{i-1} \\
2 k \phi'(i + 1) k \\
\end{array} \right\} + M \sqrt{\left(\frac{\beta}{2}\right)^2 + \beta a} - \frac{M \beta}{2} \times \left[ 1 + \frac{a_i}{\sqrt{\left(\frac{\beta}{2}\right)^2 + \beta a}} \right]
\]

at \( i = N - 1 \): \( a_N = 0, e_N = 0 \).

for \( i = 0 \):

\[
\left( \begin{array}{l}
-3 \\
2 k \phi'(i + 1) k \\
\end{array} \right\} a_i^{i+1} + \left\{ \begin{array}{l}
4 \\
\pi \phi'(0) h^2 \\
\end{array} \right\} a_0^{i+1} + \left\{ \begin{array}{l}
2 \\
K \phi'(0) \\
\end{array} \right\} a_0^{i+1} = \left\{ \begin{array}{l}
M \beta \\
2 \sqrt{\left(\frac{\beta}{2}\right)^2 + \beta a} \\
\end{array} \right\} a_i^{i+1} + \left\{ \begin{array}{l}
4 \\
\pi \phi'(0) h^2 \\
\end{array} \right\} a_i^{i+1} + \left\{ \begin{array}{l}
-4 a_i + a_i^{i-1} \\
2 k \phi'(i + 1) k \\
\end{array} \right\} + M \sqrt{\left(\frac{\beta}{2}\right)^2 + \beta a} - \frac{M \beta}{2} \times \left[ 1 + \frac{a_i}{\sqrt{\left(\frac{\beta}{2}\right)^2 + \beta a}} \right].
\]