SIMULATION OF HEAP LEACHING PROCESS BY PSPD MODEL*

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Abstract– In this study a mathematical method called PSPD (profile side-pore diffusion) based on the work of Bouffard and Dixon [10] is proposed for simulation of solute transport through the pores of a heap, considering the reaction terms. The obtained governing equations are converted into dimensionless forms and are solved by writing a computer program based on an implicit finite difference method. The solution of the model results in the outlet acid concentration profile. In order to check the accuracy of the proposed model and also for determination of effective diffusivity of sulfuric acid in copper oxide ore particles, two experimental setups are constructed, one for measurement of the effective diffusivity and the other for measuring the rate of leaching.

The effective diffusivity is obtained by two different methods which reconfirm each other. The copper oxide ore of Sarcheshmeh copper complex, situated in Kerman province in Iran, was used for experimentation. The effects of different factors such as particle size, acid solution flow rate and initial acid concentration are examined on the rate of leaching in two columns of different heights.

Comparison of the calculated data with experimental data under the same operating conditions shows a good agreement between them and hence validity of the proposed model was confirmed. The results show that the extraction time of copper is influenced mostly by increasing the acid solution flow rate and decreasing the column height due to decreasing the advection time.

Keywords– Heap leaching, mathematical model, simulation, diffusion

1. INTRODUCTION

Several attempts have been made during the last 30 years to model the heap leaching process, in which valuable metals are extracted from ore particles by percolating a leaching solution through a bed or pile of ore particles, called a heap [1]. Early models consisted of two-dimensional governing equations to describe the diffusion processes into the pore spaces of the heap. The flow and transport equations, defining the rate at which solutes travel through the bed interstices, exchange across phase boundaries and diffuse through the filling solution of the pores, now constitute the backbone of any heap leaching model [2-4]. One of the critical factors in this process is the distribution of the leaching solution through the heap and its relationship with the flow rate. A fraction of the leaching solution is assumed to be trapped in the pores of the particles in a dry ore bed. This trapped solution would progressively push the air out of the smaller void to form stagnant acid pockets by saturating the pores. Although Dixon and Hendrix [5] assumed that the trapped liquid is only in the pores of particles, Sanchez-Chacon and Lapidus [6] also accounted for a stagnant liquid film over the particles surface. Whether the acid film is uniform or contiguous or whether the stagnant pockets exist in the pores of the particles or at their interfaces, suffice it to say that the stagnant liquid fraction accounts typically for 17 to 32 percent of the void volume as measured in copper heap and columns loaded with rocks of 5 to 152 mm in size [7]. The physical

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properties of the solution and shape, size and wet ability of the particles have been found to have a significant effect on the stagnant liquid holdup as shown experimentally by Schlitt [8]. When the smaller openings are flooded, the leaching solution finds its way through the larger channels. This free draining solution percolates as rivulets and film across the surface of the particles. The amount of flowing liquid collected during drainage depends primarily on the liquid flow rate, the packing characteristics and to a lesser extent on the fluid physical properties.

The aforementioned two authors [5, 6] assumed that the flowing liquid moved vertically as a front through the bed at a constant velocity given by the product of the superficial velocity and the degree of void saturation. From a theoretical standpoint, the velocity at any given location can be calculated more accurately using Darcy’s law, which takes into account the pressure gradient associated with the hydrostatic head and the local permeability.

As pointed out by Roman and Bhappu [9] in their review of heap hydrology, a study of the hydrodynamics restricted to the notion of solution holdup and relative volumes would be incomplete without addressing the issue of solute transfer across boundaries and diffusion into stagnant pores. Dixon and Hendrix [5] have assumed a rapid mass transfer at the liquid-liquid interface and slow diffusion of solute into the pores. The transfer rate was given by the diffusional flux on the pore side of the interface. In addition to the hypothesis laid out in Dixon and Hendrix’s model, Sanchez-Chacon and Lapidus [6] have also considered the existence of film mass transfer at liquid-solid interface given by a first order linear term estimated from correlations pertaining to hydrodynamics in trickle-bed reactors. Bouffard and Dixon [10] combined the most important transport and transfer phenomena into a one-dimensional mechanistic model of the heap leaching process under forced air advection, and to evaluate its parameters from actual experimental tracer curves.

The aim of this article is to combine the works of Bouffard and Dixon [10] and Dixon et al [11], taking into account a reaction term without forced air advection. This study is divided into three parts. First, the effects of different operating factors, such as particle size, acid solution flow rate and initial acid concentration on the rate of leaching were investigated practically in two columns of copper oxide ore with different heights. Second, the effective diffusivity of sulfuric acid solution in copper oxide ore was determined experimentally, and finally, the proposed mathematical model was compared with the experimental data.

2. HEAP LEACHING PROCEDURE

Heap leaching of copper bearing mineral ores in large scale production began in the copper industry for treating oxide ore in 1970. Copper heap leaching uses a dilute sulfuric acid solution and, in the first decade of its commercialization, the environmental issues were not considered significant. Because of increasing economic and environmental concerns in the 1980’s, copper heap leaching began improving their containment items. In this process, large piles of crushed or run of mine rock (or occasionally mill tailings) are leached with various chemical solutions that extract valuable minerals. The largest installations, in terms of both land area and annual tonnage, are associated with copper mines, where copper-containing minerals are irrigated with a weak sulfuric acid solution. An acidified rich leach solution is applied to a heap at an irrigation rate of up to $15 \text{ L/hr/m}^2$. As the solution percolates through the heap, it comes into contact with the ore and a reaction occurs between the acid and the copper minerals. The copper ore used in Sarcheshmeh Copper Complex, situated in Kerman province in Iran, includes several components appearing in Table 1. Considering the high value of Malachite, $\text{Cu}_2\text{CO}_3(\text{OH})_2$, and its fast reaction with sulfuric acid (in comparison with the other components in Table 1), it could be assumed as the only component in copper ore and the main reaction is assumed to be:
This reaction results in copper dissolution in the ore and its subsequent entry then moves into an aqueous solution called pregnant leach solution (PLS). This solution is then passed down through the ore pile and is recovered at the bottom on the leach pad, which usually consists of a geomembrane liner sometimes clay (either to create a true composite liner, or more commonly as a good quality bedding layer for the geomembrane) and a permeable crushed rock drainage system called an over liner with a drainage pipe network. In some applications (principally oxide copper ores) thin liners are installed between layers or lifts of ore to intercept the PLS earlier. Copper is extracted from the PLS using electro winning processes and the acidic solution is recycled back onto the leach pile. A schematic of a heap leach system is shown in Fig. 1. The piping network for each heap includes some main lines at the ground level and heap supply header pipes along the heap; they distribute the solution over the surface of a heap through a series of sprinklers.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Composition</th>
<th>Copper wt%</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native copper</td>
<td>Cu</td>
<td>0.15</td>
<td>Copper red</td>
</tr>
<tr>
<td>Cuprite</td>
<td>Cu₂O</td>
<td>0.05</td>
<td>Red</td>
</tr>
<tr>
<td>Chalcoite</td>
<td>Cu₃S</td>
<td>0.45</td>
<td>Dark gray</td>
</tr>
<tr>
<td>Covellite</td>
<td>CuS</td>
<td>0.15</td>
<td>Indigo blue</td>
</tr>
<tr>
<td>Bronite</td>
<td>Cu₃FeS₄</td>
<td>0.05</td>
<td>Golden brown to copper red</td>
</tr>
<tr>
<td>Malachite</td>
<td>Cu₃Co₃Cu(OH)₂</td>
<td>96</td>
<td>Bright green</td>
</tr>
<tr>
<td>Azurite</td>
<td>2CuCO₃Cu(OH)₂</td>
<td>3</td>
<td>Blue</td>
</tr>
<tr>
<td>Chalcopirrite</td>
<td>CuFeS₂</td>
<td>0.3</td>
<td>Golden yellow</td>
</tr>
</tbody>
</table>

Fig. 1. Leaching process flow sheet

3. MATHEMATICAL MODELING

Based on seven different diffusional models complied and illustrated by Roman and Bhappu [9], three two-phase models (Mixed side-pore diffusion model, profile side-pore diffusion model for uniform and variable pore length) have been developed to simulate the shape of the column tracer breakthrough curves by Bouffard and Dixon [10]. Dixon et al.[11] and Sayyad Amin [12] revised these models to predict the
EFFLUENT CONCENTRATION RESPONSE OF REAGENT FROM SPENT HEAPS UNDER BOTH FRESH AND RECYCLED WATER RISING.

These models were also used by Skagius and Neretnieks [13] Stollenwerk and Kipp [14] to simulate the transport of molybdate through a 30 cm long column packed with sediment collected from an uncontaminated aquifer.

In the PSPD (profile side-pore diffusion) model, the concentration profile in the pores is controlled by a diffusional transport mechanism as illustrated in Fig. 2.

![Fig. 2. Representation of the PSPD model with uniform pore length [10]](image)

The transfer rate at the open end of the pores is then given by the diffusional flux, which depends on the concentration gradient in the stagnant phase at the interface. No transfer takes place at the closed end of the pores. The reaction between the solute and the solution is so fast that no resistance in the stagnant phase at the interface was observed. The continuity equation for the stagnant liquid phase with their initial and boundary conditions is given by:

\[
\varepsilon_s \frac{\partial c_s}{\partial t} = D^{eff} \left[ \frac{\partial^2 c_s}{\partial x^2} + \frac{n \varepsilon_s \partial c_s}{\partial x} \right] - \varepsilon_s k c_s \tag{1}
\]

**IC:** \( c_s(x,0) = 0 \)

**BC1:** \( c_s(0,t) = c_f \)

**BC2:** \( \frac{\partial c_s}{\partial x} \bigg|_{x=X} = 0 \)

Where \( D^{eff} \) is the effective diffusivity of the solute in the pores. The constant \( n \) is a diffusion factor equal to 0 for the rectangular system, 1 for the cylindrical system or 2 for the spherical system.

The continuity equation for the flowing liquid phase is written for a pore of uniform length \( X \) as:

\[
\varepsilon_f \frac{\partial c_f}{\partial t} = -u \frac{\partial c_f}{\partial z} - \frac{D^{eff} (n+1) \partial c_f}{X \partial x} \bigg|_{x=0} - \varepsilon_f k c_f \tag{5}
\]

With the following initial and boundary conditions:

**IC:** \( c_f(z,0) = 0 \)

**BC:** \( c_f(0,t) = c_i \)

In order to simplify the model equations, the following dimensionless parameters are defined:

\[
\xi = \frac{x}{X}, \ t_d = \frac{D^{eff}}{\varepsilon_s X^2}, \ C_s^* = \frac{c_s}{c_i}, \ C_f^* = \frac{c_f}{c_i}, \ \zeta = \frac{z}{Z}, \ t_a = \frac{\varepsilon_f Z}{u}, \ \Phi = \frac{\varepsilon_f}{\varepsilon_s} \tag{8}
\]

Using these dimensionless parameters, Eqs. (1), (2), (3) and (4) are rewritten as:
The governing equations of the model consist of two partial differential equations (PDEs) which are coupled together. The system of non-linear partial differential equations has been solved using an implicit finite differential method. The finite difference method of Crank-Nicolson is employed to solve initial and boundary value problems in order to replace each of the equations by central and forward approximation formula. The Gauss-Siedel method has been used for the solution of the resulting system of non-linear algebraic equations.

5. EXPERIMENTATION

a) Experimental apparatus for evaluation of the proposed model

In order to evaluate the validity of the proposed modified PSPD model, an experimental apparatus was erected. The schematic diagram of the experimental set-up is represented in Fig. 4. As is shown, this set-up consisted of a cylindrical column containing Malachite, a peristaltic pump for feeding the acid solution and two influent and effluent reservoirs. In each run, a sulfuric acid solution of a certain concentration was...
fed to the top of the column and its concentration measured at the bottom of the column at different times. Two different columns of heights, 165 cm and 382 cm with the same diameter of 25 cm, two different particles of diameter, 2.5 cm (1.9 cm < d_p < 3.15 cm) and 10 cm (8.9 cm < d_p < 10.16 cm), and two different acid concentrations of 10 and 30 g/L were used.

b) Experimental apparatus for determination of effective diffusivity

In order to measure the effective diffusivity of the acid in a horizontal bed of ore, an apparatus, as shown in Fig. 5, was erected. The apparatus consisted of a diffusional cell of PVC, a peristaltic pump for acid feeding, a conductivity cell, a data acquisition system, a Meger apparatus and two influent and effluent reservoirs. Length, height and width of the diffusion cell were 80, 30 and 30 cm, correspondingly. This system could be used in two different methods for determination of effective diffusivity as follows:

1. Method 1- Determination of effective diffusivity by electrical resistance measurement: If the transport takes place only in the pore solution, then the relation between the effective diffusivity D^eff and the bulk phase diffusivity D_v for a component can be written as [13, 14]:

\[
D^\text{eff} = D_v \frac{\varepsilon \delta_D}{\tau^2} \tag{16}
\]

where \(\delta_D\) is the constrictivity and \(\tau\) is the tortuosity of the porous material. The formation factor \(\frac{\varepsilon \delta_D}{\tau^2}\) in Eq. (16) may be obtained by measuring the electrical resistance of the rock sample when its pores are filled with water, \(R_o\), and when its pores are filled with acid solution, \(R_s\). Providing that the conduction takes place only in the liquid phase [15-17], the following equation could be written:

\[
\frac{D^\text{eff}}{D_v} = \frac{R_o}{R_s} \tag{17}
\]

The Meger apparatus was used for measurement of electrical resistances of the diffusion cell for the two different aforementioned cases. This apparatus works on the basis of applying a given amount of voltage through the sample and measuring the current induced in the sample. Since the diffusivity of liquids in porous solids is only a function of pressure, temperature and the geometry of porous solid, the zero
concentration malachite rock was used. Having the value of $D_x$ [20], $R_0$ and $R_e$ for a specified size of rock, the experimental value of $D^{\text{eff}}$ could be determined. The results obtained for the different particle sizes are shown in Fig. 6.

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{fig5}
\caption{Experimental apparatus (1-influent, 3) conductivity cell, 2- effluent, 4- data acquisition system, 5- rock sample, 6- transparent PVC chamber, 7- PVC plate, 8- hole for input liquid, 9- hole for output liquid, 10,11- Meger apparatus electrode, 12- Meger apparatus, 13- peristaltic pump with controller)}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{fig6}
\caption{Fig. 6. Effect of particle diameter on resistivity of the rock sample}
\end{figure}

2. Method 2- Determination of effective diffusivity by measuring the total amount of diffusing substance: In order to be sure of the values obtained for the effective diffusivity by the first method, a second method was proposed based on a mathematical model presented for the diffusion cell for which a schematic diagram is shown in Fig. 7 [19, 20].

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{fig7}
\caption{Fig. 7. Schematic diagram of the diffusion cell}
\end{figure}
Writing the continuity equation for a volume element of the diffusion cell, as shown in Fig. 7, will result in

$$D_{\text{eff}} \frac{\partial^2 c}{\partial z^2} = \frac{\partial c}{\partial t}$$

(18)

with the following boundary conditions:

$$BC.1 \quad \text{at } z = 0 \quad t = 0 \quad c = 0$$

(19)

$$BC.2 \quad \text{at } z = Z \quad t \to \infty \quad c = c_{\text{at}}$$

(20)

The analytical solution of this equation is given as [16]:

$$\frac{c(z,t)}{c_{\text{at}}} = 1 - \frac{z}{Z} - \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{n\pi}{Z} \sin\left(\frac{n\pi}{Z}\right) \exp\left(-\frac{D_{\text{eff}} n^2 \pi^2 t}{Z^2 \varepsilon}\right)$$

(21)

The rate at which the diffusing substance emerges from a unit area at $z = Z$ of the slab is given by:

$$N = -D_{\text{eff}} \frac{\partial c}{\partial z} |_{z=Z}$$

(22)

By integrating Eq. (21) with respect to time, the total amount of diffusing substance $M$, which has passed through the slab during the time period $t$, was obtained as:

$$\frac{M}{Z c_{\text{at}}} = \frac{D_{\text{eff}}}{Z^2} - \frac{6 \pi^2}{\varepsilon} \sum_{n=1}^{\infty} \frac{(b)^n}{n^2} \exp\left(-\frac{D_{\text{eff}} n^2 \pi^2 t}{Z^2 \varepsilon}\right)$$

(23)

As $t \to \infty$, Eq. (23) approaches the linear relation:

$$M = \frac{c_{\text{at}} D_{\text{eff}}}{Z} t - \frac{c_{\text{at}} Z \varepsilon}{6}$$

(24)

with the slope of $\frac{C_1 D_{\text{eff}}}{Z}$ and an intercept on the time axis $t = \frac{Z^2 \varepsilon}{6 D_{\text{eff}}}$. By measuring $M$ at different times, using the diffusion cell, and plotting the equation (24), the amount of $D_{\text{eff}}$ could be calculated.

The values obtained for the effective diffusivity by the two different methods are shown in Table 2 for different particles sizes.

<table>
<thead>
<tr>
<th>#Test</th>
<th>diameter (cm)</th>
<th>$D_{\text{eff}}$ (m$^2$/s) Method 1 ($\times 10^{-11}$)</th>
<th>$D_{\text{eff}}$ (m$^2$/s) Method 2 ($\times 10^{-12}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.5</td>
<td>4.1</td>
<td>3.8</td>
</tr>
<tr>
<td>2</td>
<td>7.5</td>
<td>6.1</td>
<td>5.9</td>
</tr>
<tr>
<td>3</td>
<td>10.0</td>
<td>10.1</td>
<td>10.0</td>
</tr>
<tr>
<td>4</td>
<td>12.5</td>
<td>12.0</td>
<td>12.3</td>
</tr>
<tr>
<td>5</td>
<td>15.0</td>
<td>14.1</td>
<td>14.4</td>
</tr>
</tbody>
</table>

This apparatus was also used for porosity measurement of the rocks. For this purpose, $Na NO_3$ solution was used as the volume measuring agent. The diffusion cell was filled with this solution in two different situations; namely, when the diffusion cell was full with rock particles and when the diffusion cell was empty. The difference between the two-solution volumes gives the porosity of the bed.
6. RESULTS AND DISCUSSION

In the studied process, leaching includes extraction of malachite out of ore rock and its reaction with sulfuric acid solution. As a result of this reaction, sulfuric acid was consumed, copper sulfate was produced and acid concentration decreased as it passed through the bed. So the rate of leaching could be represented by the outlet acid concentration. Different operating conditions were given to the computer program and the variation of outlet acid concentration was calculated in each case. Then, by applying the same experimental operating conditions to the apparatus, the outlet acid concentration was measured in each case. The obtained experimental and calculated results were compared to show the degree of validity of the proposed model. The following results were obtained:

a) Effect of the inlet acid concentration

Figures 8a and 8b represent the effect of inlet acid concentration on the outlet acid concentration. Two different acid concentrations of 10 and 30 $\text{g/L}$ were used in two different columns. As is seen, for any inlet acid concentration, the outlet acid concentration increased with time, finally reaching the inlet acid concentration. This shows that the percent recovery of copper decreases with time and finally reaches zero. Also, it is observed that this phenomenon is accelerated by increasing the inlet acid concentration.

Figures 8a-10b reveal that there is a good agreement between the experimental and the calculated data predicted by the proposed model.

b) Effect of particle diameter

The effect of the ore particle size on the rate of leaching is represented in Figs. 9a and 9b. As is shown, the rate of leaching increases with increasing the particle diameter, a fact that could be explained by the formation of agglomerates for the smaller particles.
c) Effect of specific flow rate

The effects of the specific flow rate of acid flowing through the bed on the rate of leaching are represented in Figs. 10a and 10b. As is shown, the rate of leaching increases with increasing the specific flow rate, which is due to the increase of the mass transfer coefficient.
7. CONCLUSION

The heap leaching process was simulated in a cylindrical column applying the PSPD model. In this model, the system was divided into two different phases: flowing phase and stagnant phase. The first one is vertical and the second is horizontal. The effective diffusivity applied in this model was calculated through two different methods, and the effect of various factors such as particle size, acid solution flow rate and the initial acid concentration on the extraction time of copper (equivalent acid sulfuric consumption) existing in two columns with different heights was investigated. The results show that, of all factors studied, the acid solution flow rate and the column height were the most influential ones. The increase of initial acid flow rate or the decrease in column height lowers the effects on the advection time and makes copper extraction from the ore faster. The increase of the particle diameter influences only the diffusion time, which has no considerable effect on copper extraction kinetics due to the independence of pore length on particle diameter. The effect of advection time is much more important than that of diffusion time since the mineral particles are considered as lumped. The main parts of porosity are the intra particle porosities which are created due to dissolution of gangue minerals in acid solution. It should be considered that the mineral grains available on the external surface of the particles would be exposed to higher acid solution concentration than those buried deep down within the ore pellets and therefore would leach faster.

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NOMENCLATURE

\( a_{\text{i}} \) total interfacial area per unit heap volume \((\text{m}^2/\text{m}^3)\)  
\( c \) concentration \((\text{g}/\text{L})\)  
\( C_{\text{f}} \) flowing phase concentration \((\text{g}/\text{L})\)  
\( C_{\text{s}} \) stagnant phase concentration \((\text{g}/\text{L})\)  
\( C_{\text{f}}^{*} \) flowing phase concentration, dimensionless  
\( C_{\text{s}}^{*} \) stagnant phase concentration, dimensionless  
\( d_{\text{p}} \) particle diameter \((\text{m})\)  
\( D_{\text{eff}} \) effective diffusivity of solute \((\text{m}^2/\text{sec})\)  
\( D \) diffusivity of solute in bulk liquid \((\text{m}^2/\text{sec})\)  
\( M \) amount of diffusing component \((\text{mol})\)  
\( N \) flow rate of solution \((\text{mol}/\text{sec})\)  
\( R_{\text{s}} \) electrical resistance of salt solution \((\Omega\text{m})\)  
\( R_{\text{w}} \) electrical resistance of salt water saturated rock \((\Omega\text{m})\)  
\( k \) reaction constant \((1/\text{sec})\)  
\( n \) geometry factor for diffusion, dimensionless  
\( Q \) specific flow rate \((\text{L}/\text{mol}^2/\text{h})\)  
\( t \) time \((\text{h})\)  
\( t_{\text{a}} \) advection time \((\text{h})\)  
\( t_{\text{d}} \) diffusion time \((\text{h})\)  
\( u \) superficial bulk flow velocity \((\text{m}^3/\text{m}^2.\text{h})\)  
\( x \) position in the pore \((\text{m})\)  
\( X \) pore length \((\text{m})\)  
\( z \) heap depth \((\text{m})\)  
\( Z \) heap height \((\text{m})\)  
\( \delta \) normalized dimensionless particle diameter
\( \varepsilon \)  
volume fraction

\( \varepsilon^+ \)  
transport porosity of matrix

\( \Phi \)  
volume ratio of stagnant to flowing liquid

\( \xi \)  
normalized dimensionless pore position

\( \zeta \)  
dimensionless depth position

\( \tau \)  
tortosity

**Subscripts**

\( f \)  
flowing liquid

\( s \)  
stagnant liquid

**REFERENCES**


