

A kinetic model for heap leaching of uranium ore considering variation of model parameters with depth of heap

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Abstract Many kinetic models for heap leaching of low grade ores have been proposed and the model parameters have been treated as constants. However, some of these model parameters change with the depth of the heap. In the present work an apparatus consisted of six columns with different heights was designed and used to simulate the leaching behavior within a 3-m-high uranium ore heap at a uranium mine in South China. It was found that the model parameters α and ω for heap leaching of the uranium ore varied with the depth of the heap, and that the relationships between α and between ω and the depth of the heap were in the form of the logistic and the quadratic functions, respectively. Furthermore, a kinetic model for heap leaching of the uranium ore considering the variation of the model parameters with the depth of the ore was proposed. The kinetic model gave the fitting precision of more than 95 % and prediction precision of more than 93 %. The present work provided an approach for establishing the kinetic model for heap leaching of low grade uranium ores.

Keywords Kinetic model · Uranium ore · Heap leaching · Model parameters · Heap depth

Introduction

Heap leaching is a technology for extraction of metals from low grade ores [1, 2]. It is an operation of solid–liquid mass

transfer between the leaching solution and the ore particles [3] and has many advantages such as low investment, short construction period, simple operation and management, low environmental contamination and so on [4].

In order to evaluate the leaching behavior of an ore, many investigators [5–14] have conducted studies on the kinetic models to describe the solid–liquid reactions. Box and Prosser [5] proposed a mathematical model for heap leaching, which showed the relationship between the recovery, particle size and porosity of the ore. Dixon and Hendrix [6, 7] developed a mathematical model for heap leaching of one or more solid reactants from nonreactive, porous, spherical ore particles in dimensionless form. Mellado and Cisternas [8] presented an alternative method for the mathematical model by Dixon and Hendrix using the analytical and numerical solutions to the differential equations for heap leaching of one or more solid reactants from porous pellets. Mellado et al. [9] used the model by Dixon and Hendrix and the analytical–numerical procedure by Mellado and Cisternas to obtain data and established the analytical models for heap leaching using constitutive equations for different particle sizes and heap heights to identify the time characteristic of heap leaching with different scales of operations. And when all these models were used to predict the recovery of metals for heap leaching, the model parameters were treated as constants.

However, for an ore heap with certain height, as the leaching reaction progresses, the pH, Eh and the concentrations of acid and metal will vary with the depth of the heap, and, under certain circumstances, the dissolved metal will precipitate [10]. Moreover, the pressure from the overlying ore particles within the heap increases with the depth of the heap and this will cause the permeability of the heap to decrease with the depth of the heap [11].

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Consequently, it is necessary to study the variation of the model parameters with the depth of the heap.

In this article, Bennett's principle [12] was used to design an apparatus consisted of 6 columns with different heights for the simulation of the leaching behavior within a 3-m-high uranium ore heap at a uranium mine in South China. The objectives are to analyze the variation of the model parameters with the depth of the heap, and to establish a kinetic model for heap leaching of uranium ore considering the variation of the model parameters with the depth of the heap.

Kinetic model and model parameters

Based on the Bernoulli equation, Dixon and Hendrix model [6, 7] and Boyce and Diprima model [15], Mellado et al. [9] proposed the following model for predicting the recovery of a metal for heap leaching:

$$R(t) = R^\infty - \left[k_\theta (n_\theta - 1) \left(\frac{u_s}{\varepsilon_b z} t - \omega \right) + R_\theta^{\infty 1 - n_\theta} \right]^{\frac{1}{1 - n_\theta}} - \left[k_\tau (n_\tau - 1) \left(\frac{D_{Ae}}{\varepsilon_0 r^2} t - \overline{\omega} \right) + R_\tau^{\infty 1 - n_\tau} \right]^{\frac{1}{1 - n_\tau}} \quad (1)$$

where $R(t)$ is the recovery at any given time t (s); R^∞ represents the recovery when $t \rightarrow \infty$; R_θ^∞ and R_τ^∞ are the recoveries for the height of the heap and the particle size, respectively, $R^\infty = R_\theta^\infty + R_\tau^\infty$; n_θ and n_τ are the orders of the reaction; k_θ and k_τ are the kinetic parameters, $k_\theta > 0$, $k_\tau > 0$; u_s is the irrigation strength ($\text{cm}^3/\text{cm}^2/\text{s}$); ε_b is the volume fraction of the leaching solution; z is the depth of the heap (cm); D_{Ae} is the effective diffusivity of the pore of the reagent ($\text{cm}^2/\text{cm}^2/\text{s}$); ε_0 is the porosity of the mineral; r is the particle radius (cm); ω is a delay which is introduced by Mellado et al. [9], it is a measure for θ , and, within the time ω , $R(t) = 0$; $\overline{\omega} = \frac{D_{Ae}}{\varepsilon_0 r^2} \frac{\varepsilon_b z}{u_s} \omega$, it stands for the delay which is a measure for τ .

As Dixon and Hendrix [6, 7] indicated, θ and τ could be determined by the following equations, respectively:

$$\theta = \frac{u_s t}{\varepsilon_b z} \quad (2)$$

$$\tau = \frac{D_{Ae} t}{\varepsilon_0 r^2} \quad (3)$$

Let $\alpha = \frac{R^\infty}{R_\theta^\infty}$, and, when $n_\theta = n_\tau = 1$, Eq. (1) becomes the following simplified form:

$$R(t) = R^\infty \left[1 - \alpha e^{-k_\theta \frac{u_s}{\varepsilon_b z} \left(t - \frac{\varepsilon_b z}{u_s} \omega \right)} - (1 - \alpha) e^{-k_\tau \frac{D_{Ae}}{\varepsilon_0 r^2} \left(t - \frac{\varepsilon_b z}{u_s} \omega \right)} \right] \quad (4)$$

For convenience of analysis and application, Eq. (4) can further be simplified to the following form:

$$R(t, z) = R^\infty \left[1 - \alpha e^{-k_\theta \left(\frac{u_s t}{\varepsilon_b z} - \omega \right)} - (1 - \alpha) e^{-k_{\tau'} \left(t - \frac{\varepsilon_b z}{u_s} \omega \right)} \right] \quad (5)$$

$k_{\tau'}$ can be determined by $k_{\tau'} = k_\tau \frac{D_{Ae}}{\varepsilon_0 r^2}$.

When conducting the fitting analysis of data, Mellado et al. [9] treated α and ω as constants and supposed that, when $t \rightarrow \infty$, $R^\infty \rightarrow 1$. But in practice, there exist canalization, sedimentation and clustering at different depths of a heap, and both the inner and the outer diffusion will be affected. As a result, the relatively large part of useful metal can not be leached out, and this means that the supposition that, when $t \rightarrow \infty$, $R^\infty \rightarrow 1$ is arguable. In fact, the leaching rate of the mineral decreases with increasing depth of the heap, and there should be a relationship between R^∞ and the depth z . Mellado et al. [16] presented a relationship like the following:

$$R^\infty = \frac{a}{b + cz} \quad (6)$$

where a , b and c are constants, and $a > 0$, $b > 0$, $c > 0$. Meanwhile, as R_θ^∞ is controlled by leaching, it varies with the depth of the heap, and, therefore, α also varies with the depth of the heap.

Moreover, as Mellado et al. [9] presented, the delay time ω is determined by the formula $\omega = \frac{3(1 - \varepsilon_h) D_{Ae} z}{u_s R^2}$, and it indicates that ω varies with the depth of the heap. Since the gravity from the ore makes the porosity ε_h decrease, $(1 - \varepsilon_h)$ increases with the depth of the heap.

The following work is to determine how the two parameters α and ω vary with the depth of the heap using column leaching experiments, and to modify the model proposed by Mellado et al. [9].

Experiments

Ore characteristics

The ore for the experiments was taken from that for heap leaching at a uranium mine in South China. Its particle sizes range from 0 to 9 mm. Its main chemical composition is shown in Table 1. As can be seen from the table, the average uranium content in the ore is about 0.177 %, and the ratio between [U(IV)] and [U(VI)] ranges from 0.45 to 0.5. The gangue minerals are mainly of silicate minerals, with the contents of SiO_2 , Al_2O_3 and CaO being 78.21, 7.13 and 2.89 %, respectively. This type of uranium ore is suitable for being leached with sulfuric acid.

Table 1 Main chemical composition of uranium ore (%)

Composition	U	FeO	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	MgO	P ₂ O ₅	MnO	CO ₂	F
Content	0.177	0.587	0.289	78.21	7.13	2.89	0.677	0.018	0.116	1.92	0.301

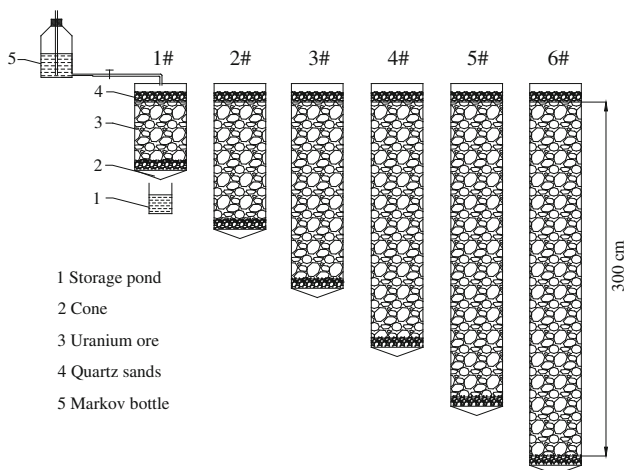


Fig. 1 Schematic diagram of the column leaching apparatus

Experimental apparatus and procedure

The column leaching apparatus, as shown in Fig. 1, consists of six acid resistant plexiglass cylindrical columns, numbered 1[#]–6[#], with their internal diameter being 88 mm and their heights being 60, 110, 160, 210, 260 and 310 cm, respectively.

In order to eliminate the end-effect, a 5-cm-thick layer of quartz sands with sizes of 1–2 mm was laid at the bottom of each column. Then the uranium ore was loaded in, and the heights of the loaded ore for columns 1[#]–6[#] were 50, 100, 150, 200, 250 and 300, respectively, and the weights of the ore for the columns were 5, 10.03, 15.08, 20.15, 25.25 and 30.40 kg, respectively. After the ore was loaded, the same 5-cm-thick layer of quartz sands was laid at the top of each column.

Before leaching experiments began, each column was washed with certain amount of water to scour off the humus and other impurities in the uranium ore until the ore became saturated. As the apparatus was simulating the leaching situation at different depths of a 3-m-high heap, the irrigation conditions for columns 1[#]–5[#] had to be the same as those for column 6[#]. The leaching solution was sulfuric acid solution in concentration of 20 g/L, and the concentration should be changed in accordance with the pH value of the pregnant leach solution (PLS) of the column 6[#], ensuring that the pH of the PLS was maintained between 1.0 and 2.0. The liquid–solid ratio was 0.1 L/kg, and, 3 L of leaching solution was used to irrigate each column and the irrigation lasted for 12 h on each day, and

Table 2 Concentrations of sulfuric acid of leaching solution during different periods of leaching

Irrigation time (d)	Concentration of sulfuric acid (g/L)	Irrigation volume per day (L/d)
1–18	20	3
19–40	15	3
41–82	10	3

the irrigation strength was 41.1 L/m²/h. Table 2 shows the sulfuric acid concentrations of leaching solution during different periods of leaching. The average concentration of sulfuric acid was 12.8 g/L for the whole process of leaching.

At the end of the irrigation on each day, samples were taken at the bottom of each column. The volume, the uranium concentration, pH and Eh of the collected PLS were measured.

Results and discussion

Variation of leaching rates of uranium with time at different depths of the heap

The variation of leaching rates of uranium with time for columns 1[#]–6[#] is shown in Fig. 2. It can be seen that the leaching rate of uranium decreases with the depth of the heap, and that, during the early stage of the leaching, the smaller the depth is, the faster the leaching rate grows.

Relationships between α and between ω and depth of the heap

It is assumed that the effective diffusivity of the reagent within the pore of the ore particles D_{Ae} , the particle radius r , the porosity of the mineral ϵ_0 , and the void fraction of the heap ϵ_h are constants, and that, when $t \rightarrow \infty$, $R^\infty \rightarrow 1$. Based on the assumption, MATLAB 6.5 Curve Fitting Tool was used to fit Eq. (5) using the experimental data of columns 1[#]–6[#], respectively, and the fitted values of α , ω and the correlation coefficients are shown in Table 3.

When fitting, the average concentration of sulfuric acid during the leaching period of 82 days was used, ϵ_b was calculated to be 0.0075, and u_s , 49.35 cm³/cm²/d. As the

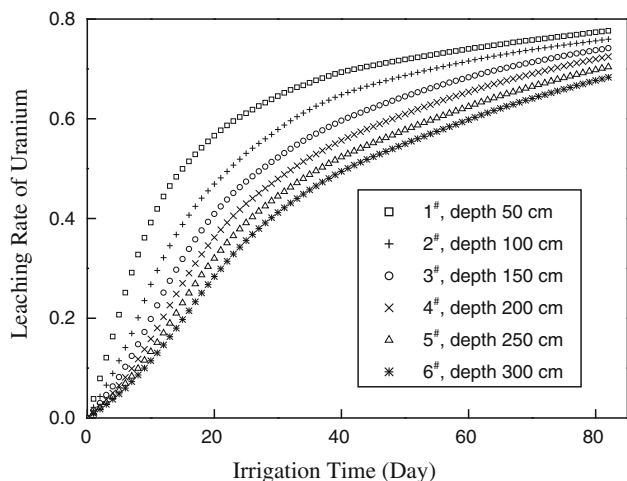


Fig. 2 Variation of leaching rates of uranium with time for columns 1#–6#

variation of constants k_θ and $k_{\tau'}$ was not significant and their values could be chosen arbitrarily [17], k_θ and $k_{\tau'}$ were assumed to be 0.0001, 0.0001, respectively. α and ω should take values from the ranges set by $\alpha \in [0, 1]$ and $\omega \in [0, \infty)$, respectively.

It is obvious that α decreases with the depth of the heap, and that its variation follows the S-type curve. Considering $\alpha \in [0, 1]$, the relationship between α and the depth of the heap can be assumed to be the logistic function:

$$\alpha = \frac{A_1 - A_2}{1 + (z/z_0)^p} + A_2 \tag{7}$$

It can also be seen that ω increases with the depth and convexes upward if the depth is defined as the horizontal ordinate. As a result, the relationship between ω and the depth of the heap can be assumed to be the quadratic function:

$$\omega = mz^2 \tag{8}$$

Fig. 3 Fitted surface

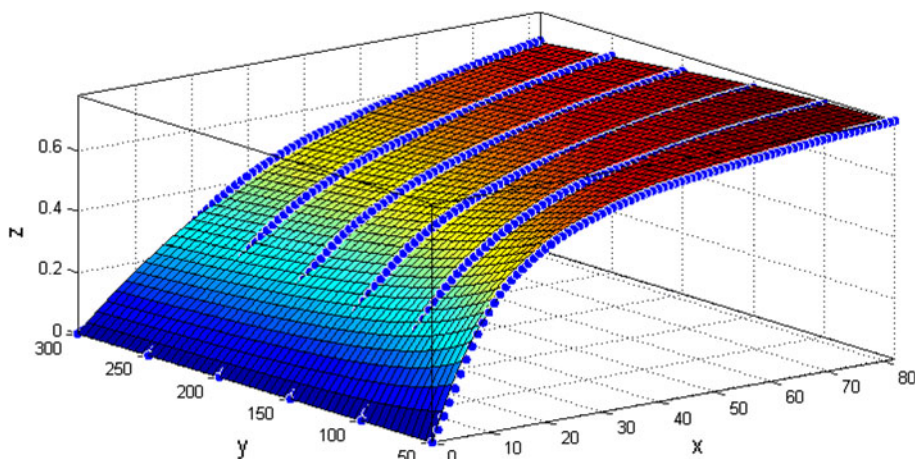


Table 3 Fitted values of α , ω and their correlation coefficients

Heap depth(cm)	α	ω	R^2
50	0.7443	9.59E - 06	0.9963
100	0.7401	9.249	0.9884
150	0.7389	10.97	0.9989
200	0.7254	18.42	0.9984
250	0.7202	20.47	0.9987
300	0.7182	28.32	0.9987

Modified kinetic model for heap leaching of uranium

By substituting Eqs. (6)–(8) into Eq. (5), the modified kinetic model for heap leaching of uranium ore considering the variation of the model parameters with the depth of the heap can be established:

$$R(t, z) = \frac{a}{b + cz} \left[1 - \left(\frac{A_1 - A_2}{1 + (z/z_0)^p} + A_2 \right) e^{-k_\theta \left(\frac{us}{b^2} - mz^2 \right)} - \left(1 - \left(\frac{A_1 - A_2}{1 + (z/z_0)^p} + A_2 \right) \right) e^{-k_{\tau'} \left(t - \frac{mb}{us} z^3 \right)} \right] \tag{9}$$

In order to determine the constants, Eq. (9) should be fitted using the experimental data from columns 1#–6#. It should be pointed out that all the experimental data from columns 1#–6# were simultaneously used for the fitting and the equation can then be used for interpolating.

Before fitting, it was assumed that $a \in (0, \infty)$, $b \in (0, \infty)$, $c \in (0, \infty)$, $k_\theta \in (0, \infty)$, $k_{\tau'} \in (0, \infty)$, $A_1 \in (0, 1)$, $A_2 \in (0, 1)$, $p \in (0, \infty)$, $z_0 \in (50, 300)$, $m \in (-\infty, \infty)$. The fitting was conducted using MATLAB 6.5 Surface Fitting Tool, and the constants were determined to be $a = 1716$, $b = 213$, $c = 4.433e - 6$, $k_\theta = 0.0004318$, $k_{\tau'} = 0.02814$, $A_1 = 0.6663$, $A_2 = 0.4116$, $p = 0.3131$, $z_0 = 206.1$, $m = -2.441e - 14$. The fitted surface is shown in Fig. 3,

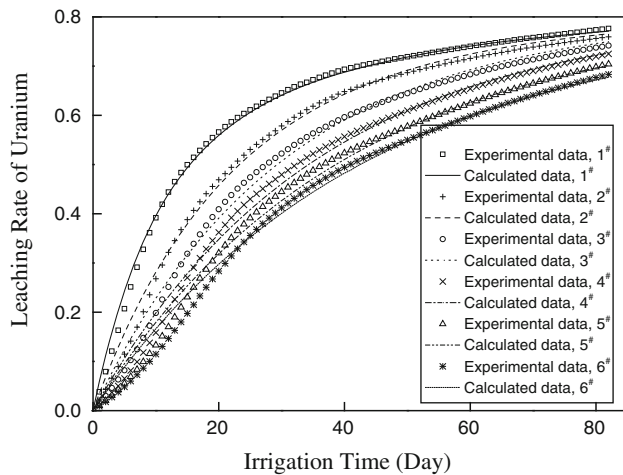


Fig. 4 Comparison between the leaching rates from experiments and fitted equation

where X , Y and Z represent the irrigation time, the depth of heap and the leaching rate of uranium, respectively, and the correlation coefficient was 0.9944. Obviously, the fitted surface well reflects the variation of leaching rate of uranium with time at different depth of the heap.

Validation

In order to check the fitting precision, the leaching rates from columns 1[#]–6[#] were compared with the calculated leaching rates from Eq. (9) for columns 1[#]–6[#] and the comparison results are shown in Fig. 4. The errors between the leaching rates from leaching experiments and the fitted equation for columns 1[#]–6[#] are 0.03, 0.036, 0.0349, 0.0158, 0.023 and 0.0477, respectively.

Furthermore, in order to check the prediction precision, another column leaching experiment was conducted. All the leaching conditions for this column leaching experiment were the same as those for column 6[#] leaching experiment except that the height of the loaded uranium ore was 120 cm and the weight was 12.05 kg. Equation (9) was used to predict the leaching rate for the experiment. The comparison result between the predicted leaching rates and the experimental results is shown in Fig. 5. The error between the model predicted and the experimental leaching rates for the 120-cm-high column is 0.0672.

Conclusions

- (1) The apparatus consisted of six columns with different heights is suitable for conducting leaching experiments simulating the leaching behavior within a 3-m-high uranium ore heap.

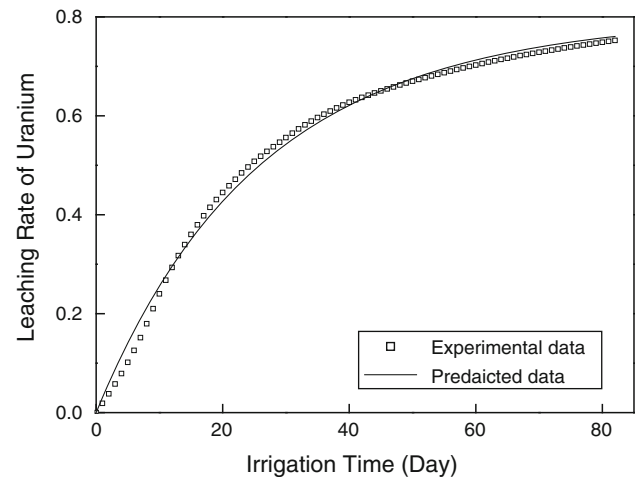


Fig. 5 Comparison between the model predicted and the experimental leaching rates for the 120-cm-high column

- (2) The leaching experimental results show that the model parameters α and ω for the model proposed by Mellado et al. vary with the depth of the heap. The relationships between α and between ω and the depth of the heap are in the form of the logistic and the quadratic functions, respectively.
- (3) A kinetic model is proposed for heap leaching of uranium ore considering the variation of the model parameters with the depth of the heap by modifying the model proposed by Mellado et al. using the relationships between α and ω and the depth of the heap.
- (4) The proposed kinetic model gives as high as 95 % fitting precision and as high as 93 % prediction precision.
- (5) The present work provides an approach suitable for establishing the kinetic model for heap leaching of uranium ore considering the variation of the model parameters with the depth of the heap.

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