Research Article

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Influence of Chemical Osmosis on Solute Transport and Fluid Velocity in Clay Soils

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Abstract: Solute transport through the clay liner is a significant process in many waste landfills or unmanaged landfills. At present, researchers mainly focus on the test study about semi-membrane property of clay material, however, the influence of chemical osmosis caused by membrane effect on solute transport and fluid velocity is insufficient. In this investigation, based on the classical advection-diffusion equation, a one-dimensional solute transport model for low-permeable clay material has been proposed, in which the coupled fluid velocity related with hydraulic gradient and concentration gradient is introduced, and the semi-membrane effect is embodied in the diffusion mechanism. The influence of chemical osmosis on fluid velocity and solute transport has been analyzed using COMSOL Multiphysics software. The simulated results show that chemical osmosis has a significant retarded action on fluid velocity and pollutant transport. The proposed model can effectively reveal the change in process of coupled fluid velocity under dual gradient and solute transport, which can provide a theoretical guidance for similar fluid movement in engineering.

Keywords: chemical osmosis; semi-membrane; diffusion; solute transport.

1 Introduction

It is well known that clay materials can exhibit semi-permeable membrane behavior, which has been proven by large amount of indoor and on-site experiments [1-11]. Technical researchers typically pay more attention to the influence of clay membrane behavior on practical engineering, i.e. solid waste landfill, geothermal exploitation, nuclear waste disposal, intrusion of saltwater, and so on. When different concentrated chemicals exist on both sides of clay soils, due to the permeable membrane behavior of clay, it only allows the passage of water molecules while preventing chemicals under the concentration gradient to dislocate. The water molecules in low concentration solution will move to the high concentration solution to maintain bilateral concentration balance. The process of water flow due to concentration gradient is called chemical osmosis. The osmotic efficiency coefficient $\omega$ is usually used to demonstrate the ideal condition of clay as a semi-membrane material.

The concept of the osmotic efficiency coefficient was first proposed by Staverman [12], which was defined by the ratio of osmosis pressure measured value and the theoretically calculated value, under constant temperature. This concept has since been used to explain the osmotic mechanism in engineering practices. The investigation of Garavito [3] and Cruchaudet [4] showed that the osmotic efficiency coefficient decreases with the increase of solution concentration. Shackelford’s research group [8-10] conducted research on the measurement of the osmotic efficiency coefficient, the influence factors such as solution ions, solution concentration, clay mineral types and other factors. In addition, Zuo and Wu et al. [13-16] conducted some indoor experiments with clay materials to study the osmotic efficiency coefficient in different areas in China. Some researchers focussed on the influence of the osmotic efficiency coefficient on contaminant transport [17-20]. Their results indicated that chemical movement was hindered when $\omega$ value increased. Baechler [21] performed numerical simulations on the chemical migration with viewing $\omega$ value as the function of solute concentration. The simulated results showed that the relationship between $\omega$ value and solute concentration had a significant influence on solute transport. Liu et al. [22] proposed a coupling
dynamic model of solute transport, considering the effect of membrane behavior and cation exchange, the results indicated that the chemiosmosis in geo-synthetic clay liner (GCL) could effectively delay the solute transport velocity. It is noteworthy that in the process of solute transport, the retardation effect due to chemiosmosis increases with the decrease of the solute concentration. Sun et al. [16] proposed that chemical osmosis was the key factor affecting the pore water movement and it even exceed hydraulic head. Thus chemical osmosis is of significance to control the concentration distribution with time and space of contaminant and it will change the breakthrough flux of solute. However, the influence mechanism of chemical osmosis to pore water flow has not been analyzed by researchers. Most importantly, there is less quality evaluation of results and discussion about the intrinsic mechanism of the chemical osmosis effect on contaminant transport process.

The aim of the study is to propose a 1D contaminant transport model for low permeability clay media based on the classical convection-diffusion equation. The combined driving action of hydraulic gradient and concentration gradient is taken into consideration, and the coupled fluid velocity caused by the hydraulic gradient and the concentration gradient is introduced. Furthermore, the diffusion mechanism incorporates the semi-membrane effect of clay material. The COMSOL Multiphysics software is used to conduct a numerical simulation to investigate the chemical osmosis on pore fluid flow and solute transport. The numerical results can afford a theoretical support for multi-physics fields coupled process.

2 Modified solute transport model

The classical 1D convection-diffusion model of solute transport can be described by the following equation,

\[
R_o \frac{\partial c}{\partial t} = -\nabla \cdot J_v + D \frac{\partial^2 c}{\partial z^2}
\]  

(1)

where \( R_o \) is the retardation factor of clay to chemicals. It can be expressed as \( R_o = 1 + K_n \frac{\rho_s}{\rho_c} \) under linear pattern of adsorption, where \( K_n \) is the adsorption coefficient; \( \rho_s \) is the density of solid; \( c \) is the contaminant concentration; \( J_v \) is the solute flux due to convection; \( D \) is the effective diffusion coefficient of chemicals.

When the semi-permeability membrane of clay media is taken into account, the solute flux due to convection can be given by the following,

\[
J_v = (1 - \omega) v_f c
\]  

(2)

where \( v_f \) is the true velocity of pore fluid across the clay. The relationship between true velocity and average velocity is given as the following,

\[
v_f = \frac{v}{n}
\]  

(3)

where \( n \) is the porosity and \( v \) is the average velocity or Darcy velocity. If the hydraulic gradient and chemical concentration gradient exist simultaneously, the flow of pore fluid will be driven by dual gradient.

\[
v = k_h i_h + k_c i_c
\]  

(4)

where \( k_h \) is the hydraulic coefficient; \( i_h \) is the fluid hydraulic gradient; \( k_c \) is the chemical hydraulic coefficient and \( i_c \) is the chemical concentration gradient. The chemical hydraulic coefficient and chemical concentration gradient can be written as

\[
k_c = \omega k_h
\]  

(5)

\[
i_c = \frac{1}{\gamma_w} \frac{\partial \pi}{\partial z}
\]  

(6)

where \( \gamma_w \) is the unit weight of pore water and \( \pi \) is the osmotic pressure.

For the contaminant with anionic and cationic valency 1:1, the osmotic pressure can be approximately expressed by Vander Hoff formula when the concentration value of contaminant is less than 1 M/L.

\[
\pi = RTc
\]  

(7)

where \( R \) is the universal gas constant and \( T \) is the absolute temperature.

Because the pore channels of clay are different in shape, the diffusion coefficient of contaminant is generally less than that in free water. In general, the effective diffusion coefficient of contaminant in soil can be written as [8]

\[
D = \tau (1 - \omega) D_0
\]  

(8)

\[
\tau = n^m
\]  

(9)

where \( \tau \) is the tortuosity factor [23]; \( D_0 \) is the diffusion coefficient of contaminant in free water and \( m \) is the empirical coefficient.
Substituting Eqs.(2)-(9) into Eq.(1) yields,

\[
\left(1 + \frac{K_d}{M} \right) \frac{\partial c}{\partial t} = -\nabla \cdot \left( \left(1 - \omega \right) \frac{k_h}{\gamma_w} \frac{\partial c}{\partial z} \right) + \kappa \frac{\partial c}{\partial z} c_{\text{in}}^{\rho} \frac{\rho}{\partial z} \left(1 - \omega \right) \frac{\partial c}{\partial z}
\]  

(10)

where \( M \) is the molar mass of contaminants.

Eq.(10) is the convection-diffusion equation of 1D contaminant transport considering chemical osmosis effect under the combined action of a hydraulic gradient and concentration gradient.

### 3 Numerical simulation

#### 3.1 Transport system of solute in clay liner

Figure 1 shows a schematic representation of clay liner. It can be seen that the leachate produced by the waste decomposition will leak into the clay soils, and further break through the clay liner into the ground water, which will result in a potential danger of ground water contamination.

#### 3.2 Solution conditions and model parameters

The model simulations were carried out using COMSOL Multiphysics software. The research object is the clay liner with depth 1m. Sodium chloride (NaCl) solution is taken as the contaminated source with constant concentration.

The Cauchy boundary condition is occupied in the numerical simulation as follows:

Initial conditions: \( c(z, 0) = 0, \quad (0 < z < 1 \text{m}) \)

Boundary conditions: \( c(0, t) = c_{\text{in}}, \quad (z = 0, t \geq 0) \);

\( \lambda \frac{\partial c}{\partial z} + \mu c = 0, \quad (z = 1, t \geq 0) \)

where \( \lambda \) and \( \mu \) are the Cauchy condition parameters. In this study, \( \mu/\lambda = 0.1 \text{m}^{-1}[24] \), \( \lambda = 17.37 \text{m}^{-1} \) [25].

#### 3.3 Simulation results

In order to study the influence of chemical osmosis on contaminant transport, the proposed convection-diffusion equation is solved by COMSOL Multiphysics software. The results include two cases (considering chemical osmosis and ignoring chemical osmosis), in which the convection-diffusion equation ignoring chemical osmosis is as following:
\[
\left(1 + K_i \frac{\rho_i}{n}\right) \frac{\partial c}{\partial t} = -\nabla \cdot \left[\left(1 - \omega\right) \frac{k_i c}{n}\right] + n^w \left(1 - \omega\right) D_k \frac{\partial^2 c}{\partial x^2} \tag{11}
\]

3.3.1 Influence of chemical osmosis on solute transport and fluid velocity

The NaCl concentration at the upper boundary of clay liner is 0.04 mol/L, the hydraulic gradient is 3 [27]. The concentration distributions results of NaCl with depth considering chemical osmosis and ignoring chemical osmosis are shown in Figure 2. It can be seen that at the same transport time and any soil depth, the contaminant concentration considering chemical osmosis is obviously smaller than that ignoring chemical osmosis, which shows that the chemical osmosis has a significant retardation effect on contaminant transport. The main reason is that the NaCl concentration in the pore fluid of soil is less than that of the external concentration of the soil. The concentration difference inside and outside clay will cause semi-permeable membrane effect, thus the pore water will flow from a low concentration to high concentration area under the driving force of a concentration gradient. It is noteworthy that the water movement under the concentration gradient is opposite to that of water movement under the hydraulic gradient, which can delay the contaminant migration.

The evolution of NaCl concentration with time on the bottom boundary of the clay liner has been shown in Figure 3. It can be seen that the accumulated concentration values, considering chemical osmosis effect, are less than those ignoring chemical osmosis effect at any time. Furthermore, the concentration difference caused by considering chemical osmosis versus ignoring chemical osmosis increases with the time elapsed. For example, the concentration difference reaches 0.006 mol/L when transport time reaches 20 years, which is 16% of input NaCl concentration. According to the quality standard for ground water of People’s Republic of China, the drinking water standard III for chloride is 0.25 g/L. The breakthrough time of NaCl ignoring chemical osmosis is 10.18 years, however, it reaches 12.24 years when considering chemical osmosis. The results show that the breakthrough time considering chemical osmosis reduces by 20% under the same simulated condition.

The distributions of pore fluid velocity with soil depth at different transport time are shown in Figure 4.

It can be seen from Figure 4 that chemical osmosis has a significant effect on seepage velocity. Over time, due to weaker chemical osmosis, the effect of the reduction gradually decreases with the decrease of concentration difference between internal and external clay soil. When the chemical osmosis effect is not considered, the pore fluid movement is only caused by the hydraulic gradient, thereby the velocities are determined and controlled by hydraulic conductivity and head difference. The hydraulic conductivity coefficient \(k_h\) is constant when soil structure is stable. Then the seepage velocity will keep constant under the fixed hydraulic gradient. The calculated seepage velocity reaches 9.5 cm/year as illustrated in Figure 4 (green line). It is noteworthy that the seepage velocities change under the chemical osmosis effect. At the early stage (i.e. 1 year) the seepage velocity at 0.1 m soil depth is negative (shown with black line), which indicates the chemical osmosis at the upper soil is more intense. The main reason is that most of the contaminant ions have not entered into the soil layer at the early stage, the concentration difference between internal and external...
of the upper soil reaches the extreme state, which means that the difference reaches the maximum value. Therefore, the chemical osmosis effect induced by the concentration gradient is strongest. According to the membrane effect, the water will flow from low concentration to high concentration, and the water velocity from internal to external soil is even more than the water velocity flowing into the internal soil caused by head difference, so the overall apparent velocity appears negative. As the time goes on, the contaminant ions enter the soil continuously, which leads to concentration difference; the internal and external concentration of soil gradually decreases. At the macroscopic scale, the downward flow velocity induced by hydraulic gradient becomes the dominate factor, thereby the overall velocity values are positive. It can be seen that at different simulated migration times (1 year, 5 years, 10 years and 20 years), the total velocity is less than that obtained when ignoring chemical osmosis. The results show that the inhibitory effect of the concentration gradient on velocity is still present in soil, and the influence weakens gradually as the time elapses. In addition, the inhibitory action of chemical osmosis on total flow velocity gradually decreases with the increase of soil depth, which means the values of chemical osmosis velocity induced by concentration difference of internal and external soil layer decrease gradually.

### 3.3.2 Influence of contaminant concentration on solute transport and fluid velocity

The concentration difference is a necessary condition for the chemical osmotic flow. The contaminant concentration values of the upper boundary of the soil layer will directly affect the contaminant concentration difference between internal and external soil layer, and further affect the exertion of the chemical osmosis effect. In order to quantitatively evaluate the influence of the initial input concentration of contaminant on fluid velocity and contaminant migration, 4 cases with different solute concentrations (0.01 mol/L, 0.02 mol/L, 0.03 mol/L and 0.04 mol/L) at the upper boundary of soil were studied. Since the initial contaminant concentration was different, the ordinate was chosen to be dimensionless in order to obtain the consistent simulation results. It can be seen in Figure 5 that the cumulative values of contaminant concentration show a decreasing trend with the increase of initial concentration of contaminant. The higher the contaminant concentration, the larger the concentration difference between inside and outside of the soil. Thereby the stronger the chemical osmosis effect induced by contaminant concentration, the more obvious the reverse inhibition action on velocity. In the end the strong inhibition action to contaminant transport causes the downward flux of contaminant to decrease (shown in Figure 6). Figure 6 shows that the seepage velocities of pore fluid are positive when initial concentration is less than 0.03 mol/L, which indicates that the seepage direction of pore fluid is consistent with the contaminant migration, and the promoting action of hydraulic gradient

### Table 2: Breakthrough time of pollutant under different initial pollutant concentration.

| c₀ (mol/L) | 0.01 | 0.02 | 0.03 | 0.04 |
|------------|------|------|------|------|
| Breakthrough time (year) | 10.41 | 10.85 | 11.38 | 11.97 |
on contaminant migration is greater than that of slowing down of chemical osmosis on contaminant migration.

In this investigation, the breakthrough condition of contaminant is $c/c_0\times100\% = 10\%$ according to the judgement standard put forward by Zhang et al [24]. The calculated breakthrough times of contaminant with 4 kinds of concentration are shown in Table 2. The results show that the time for contaminant to break through clay liner increases with the increase of initial concentration of contaminant. When the contaminant concentrations at the upper boundary reach 0.02 mol/L, 0.03 mol/L and 0.04 mol/L, the elongation ratio of breakthrough time reaches 4%, 9% and 15%, respectively, individually compared with the upper boundary concentration 0.01 mol/L.

4 Conclusions

Based on the classical convection-diffusion equation, the 1D contaminant transport model for low-permeability clay medium has been proposed. The chemical osmosis mechanism due to the semi-permeable membrane of clay, linear adsorption pattern, and the coupled fluid velocity under the combining driving action of hydraulic and concentration gradient, are considered. A series of numerical simulations have been carried out using COMSOL Multiphysics software. The results suggest that:

(1) Compared with pore fluid velocity induced by the hydraulic gradient, the chemical osmosis effect has obvious reverse inhibition action on fluid velocity.

(2) The direction of fluid velocity produced by chemical osmosis is opposite to that produced by water head, which plays an inhibited action on solute transport and causes the prolongation of the breakthrough time.

(3) The higher the upper boundary contaminant concentration, the stronger the chemical osmosis effect and the lower the contaminant migration velocity.

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