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# A multi-ion diffusion model through clay barriers under combined action of chemical and diffusion potential

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**Abstract:** Diffusion is an important phenomenon that governs contaminant transport through compacted clay liner at the bottom of landfill. The diffusion process is influenced by many factors, i.e., type, valence and concentration of ions. Therefore, an accurate diffusion model is of great importance for the design of liner system of landfill. The simplified Guntelberg activity coefficient was introduced to indicate concentration difference between ideal solution and actual solution. The driving force of diffusion usually considered combined action of chemical and diffusion potential. The semipermeable membrane effect of clay was considered. A diffusion model describing simultaneous movement of multi-ions through clay barrier was proposed. Moreover, the multi-physical field simulation software COMSOL Multiphysics was employed for conducting simulations for the proposed diffusion model. The results indicate that the factors such as solution non-ideality, diffusion potential, and semipermeable membrane effect of clay play an important role in the diffusion process of multiple ions. A remarkable retarded behavior was captured, when the solution non-ideality or semipermeable membrane effect was considered in the proposed model. Further, an accelerating effect on cations was observed taking diffusion potential into consideration. The multi-ion diffusion process under combined action is not a simple superposition of single influence mechanism, but rather, each mechanism restricts each other and affects the multi-ion diffusion behavior.

**Keywords:** multiple ions; activity coefficient; diffusion potential; semipermeable membrane effect; diffusion

## 1 Introduction

Landfill is the main treatment for solid waste in China. It is vital to design a liner barrier to prevent the pollution of leachate to the surrounding soil and water[1–2]. Due to the low permeability, compacted clays are often chosen as buffer material of landfill liners, in which the ion diffusion is the dominant mechanism in the solute transport[3–9]. To date, most of the diffusion models are based on the classical Fick's first law, in which is the self-diffusion coefficient is replaced by effective diffusion coefficient. However, it is well known that the effective diffusion coefficient is not a constant and varies with different ions species, environment conditions and soil properties, which leads to the limitation of choosing an appropriate diffusion coefficient. Therefore, how to predict the migration of leachates correctly and to evaluate the service efficiency of compacted clay liner need to be urgently addressed.

The phenomenon of multi-ion coexisting is common in practice. The factors like existing environment, kind of ions, the interaction of ions and clay properties should be considered in the diffusion mechanism. Debye and Huckel made mention that, the electrostatic interaction between ions can cause electrolyte solution to deviate from its ideal station and they gave an empirical expression of the activity coefficient[10–11]. Wang et al.[12] established the theory of electrolyte solution based on the concept of entropy effect, which proved that the electrostatic interaction was the main reason for the deviation of electrolyte solution from ideal solution. Most researchers made use of classical Fick's law to study the multi-ion diffusion, the influence of all the factors included a non-ideality on diffusion mechanism was embodied by the diffusion coefficient, which brought difficulty to determine the contribution of certain factor. Samson et al.[13] presented an extended Nernst-Planck diffusion model to investigate the activity of solution non-ideality, the results showed that the influence of the chemical activity couldn't be ignored. Based on the Maxwell-Stefan diffusion model, Ju et al.[7] introduce activity coefficient to propose a diffusion model for multiple ions. According to the energy balance theory, the diffusion driving force is equally the same as the friction force, Maxwell et al. put forward the Maxwell-Stefan diffusion model, in which chemical potential gradient was been used instead of concentration gradient. The Maxwell-Stefan model has an advantage of concluding the contribution of solution non-ideality, yet it is difficult to find the solution due to the nonlinear relationship between flux and measurable concentration. Thus, in most of models the activity coefficient is set to 1 for simplification[14]. For each ion, the self-diffusion process depends on the self-diffusion coefficient, which is related with the valence of ion, electro-conductibility of ion and so on[15–16]. In the multiple ion environment, the different velocity of ions will lead to an unbalanced charge development. Each ion movement suffer the action of other ions around it which can produce electrical potential called diffusion potential. Under the action of diffusion potential, the fast ion will be slowed down and the slow ion will speed up. This make the ions cluster together to maintain the electroneutrality in solutions[17–19]. Ben-Yaakov and his co-worker[20–21] conducted a diffusion test, the results showed that diffusion process was not only related with self-diffusion

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coefficient, but also related with diffusion potential. Applo et al.[22–23] used Nernst-Plank equation to study the multi-ion diffusion, in which the diffusion potential was considered. Muniruzzaman et al.[24–27] studied the multi-ion diffusion behavior under ideal condition based on Fick's law, in which the electrical coupling between ions was considered.

In addition, most solute transport models have considered the semi-permeable membrane effect of clay. The clay particles carry a net negative charge on their surfaces due to the isomorphous substitution during the formation of clay minerals. Due to the electrostatic forces, the diffuse double layer containing water molecules and cations develops at the vicinity of the clay particle surface. When the double diffuse layers of adjacent clay particles overlap, the clay can act as a semi-permeable membrane[28]. Malusis et al.[29–31] coupled the diffusion flux and membrane effect, the results showed that the diffusion flux decreased with the increase of membrane effect. The membrane effect of clay causes a retarding effect on the ion diffusion, so many researchers used retarding factor to indicate the membrane effect[32–35]. Zhang et al.[9, 36–39] considered the membrane effect of clay in their coupled modelling of solute transport.

To the best of the authors' knowledge, the influencing factors for ion diffusion has been intensively studied; however, there is limited research about the ion diffusion process considering the combined actions of multiple influencing factors. In this study, based on the generalized linear diffusion flux equation considering both the chemical potential and the diffusion potential as driving forces, a multi-ion diffusion model under combined actions through clay barriers has been proposed. The simplified Guntelberg activity coefficient was introduced to indicate the difference in concentration of the ideal and non-ideal solutions. In addition, as the semi-permeable membrane effect of clay was also studied. The advantage of the proposed model over the Fick's first law is that all the influencing factors can be determined, not using a single lumped parameter, i.e. the effective diffusion coefficient. The proposed model has been validated against previous studies in the literature. The software COMSOL Multiphysics was employed to conduct numerical simulations to demonstrate the diffusion process of multiple ions through clay barriers considering actions of different influencing factors individually or in a combined way.

## 2 Mathematical model

### 2.1 Diffusion flux equation in solution

Diffusion of chemical species in ideal free-solution typically is assumed to occur according to Fick's first law, which can be written as[3]

$$J_i = -D_i \nabla c_i \qquad (1)$$

where $J_i$ is the diffusion flux of ionic species $i$; $D_i$ is the diffusion coefficient of ion $i$; and $c_i$ is the concentration of ionic species $i$ in solution.

### 2.2 Diffusion flux equation in saturated porous media

Due to the pore structure of saturated porous media, diffusion pathways in saturated porous media are more tortuous than in free-solution. In addition, the diffusion fluxes are less in saturated porous media than in free-solution because solid particles occupy part of the cross-section area. Therefore, the tortuosity and porosity should be considered in the diffusion flux equation for the migration of chemicals in saturated porous media. Then the Fick's fist law can be modified as follows

$$J_i = -n\tau D_i \nabla c_i \qquad (2)$$

where $n$ is the porosity of porous media; and $\tau$ is the tortuosity factor.

### 2.3 Effect of solution non-ideality on diffusion flux

The electrostatic interaction among coexisting multiple ions will result in the icon concentrations different from those in the ideal state. In fact, the electrostatic interaction occurs among still or moving ions. Thus, the activity coefficient can be introduced to Eq. (2) to account for the non-ideal solution as follows[40]

$$J_i = -n\tau D_i \nabla\left(\gamma_i c_i\right) \qquad (3)$$

where $\gamma_i$ is the activity coefficient of ion species $i$.

There have been several estimation expressions of activity coefficient proposed in the literature. The extended Debye-Huckel law was chosen for the sake of simplicity[41],

$$\lg\gamma_i = -\frac{Az_i^2\sqrt{I}}{1+Ba_i\sqrt{I}} \qquad (4)$$

$$I = \frac{1}{2}\sum_i c_i z_i^2 \qquad (5)$$

where $A$ is a temperature-dependent constant for a given solvent; $z_i$ is the valence of ion $i$; $I$ is the ionic strength of the solution; $B$ is a parameter related to dielectric constant of water; and $a_i$ is a parameter related to the hydrated radius of ion $i$.

However, Eq. (4) applies to low concentration solutions. Also, the usage of Eq. (4) is limited by the difficulties associated with the determination of constants $A$, $B$, and $a_i$. The extended Debye-Huckel law has been simplified by Guntelberg with specific constants as follows[42]:

$$\lg\gamma_i = -\frac{0.51z_i^2\sqrt{I}}{1+\sqrt{I}} \qquad (6)$$

### 2.4 Effect of diffusion potential on diffusion flux

In the multi-ion coexisting case, the different diffusion velocities of anions and cations will cause a local charge unbalance in the solution. The movement of ions is influenced by the diffusion potential gradient, such that the local and global electroneutrality are maintained in the solution[43]. The experimental results showed that the diffusion potential gradient tends to slow down the faster ion and to speed up the slower ion[20]. In this study, the effect of the diffusion potential gradient was taken into consideration. Thus, the extended model is given by

$$J_i = -n\tau D_i\left[\nabla(\gamma_i c_i) + \frac{Fc_iz_i}{RT}\nabla\varphi\right] \tag{7}$$

where $F$ is Faraday's constant; $R$ is the gas constant; $T$ is the absolute temperature; and $\varphi$ is the electrical potential.

To solve Eq. (7), an additional condition needs to be supplied by the no electrical current requirement[17]

$$\sum_{i=1}^{N} z_iJ_i = 0 \tag{8}$$

where $N$ is the total number of ion species. Substituting Eq. (7) into Eq. (8) leads to

$$\nabla\varphi = \frac{-\sum\limits_{i=1}^{N} z_iD_i\nabla(\gamma_ic_i)}{\sum\limits_{i=1}^{N}\left(z_i^2FD_ic_i\right)\Big/RT} \tag{9}$$

Then, substituting Eq. (9) into Eq. (7) yields

$$J_i = n\tau\left[-D_i\nabla(\gamma_ic_i) + \frac{\sum\limits_{j=1}^{N} z_jD_j\nabla(\gamma_jc_j)}{\sum\limits_{j=1}^{N} z_j^2D_jc_j}z_iD_ic_i\right] \tag{10}$$

### 2.5 Effect of membrane effect on diffusion flux

Due to the anion exclusion and the generated diffusion double layer of ions, compacted clays can function as a semi-permeable membrane, which implies that the re-saturation of compacted clays involves predominantly the movement of water molecules and not the solute molecules. The membrane effect can be quantified by the osmotic efficiency, which is related to the confinement and the solution concentration[44]. For the multi-ion diffusion through saturated clays, the membrane effect can be included in the diffusion flux equation as given below:

$$J_i = n\tau(1-\omega)\left[-D_i\nabla(\gamma_ic_i) + \frac{\sum\limits_{j=1}^{N} z_jD_j\nabla(\gamma_jc_j)}{\sum\limits_{j=1}^{N} z_j^2D_jc_j}z_iD_ic_i\right] \tag{11}$$

where $\omega$ is the osmotic efficiency coefficient. The osmotic efficiency varies from zero to unity, which is a measurement of the degree to which the clay functions as an ideal semi-permeable membrane.

### 2.6 Proposed multi-ion diffusion model

For each ionic species, the law of mass conservation requires

$$\frac{\partial(n\gamma_ic_i)}{\partial t} + \nabla J_i = 0 \tag{12}$$

Substituting Eq. (11) into Eq. (12) yields

$$\gamma_i\frac{\partial c_i}{\partial t} + c_i\frac{\partial\gamma_i}{\partial t} + \tau(1-\omega)\nabla\left\{-D_i(\gamma_i\nabla c_i + c_i\nabla\gamma_i) + \frac{z_iD_ic_i}{\sum\limits_{j=1}^{N} z_j^2D_jc_j}\sum_{j=1}^{N}\left[z_jD_j(\gamma_j\nabla c_j + c_j\nabla\gamma_j)\right]\right\} = 0 \tag{13}$$

Equation (13) is the proposed model for the multi-ion diffusion combined actions through clay barriers under the combined actions of chemical and diffusion potential. The saturated clay barrier was assumed to be non-deformable in this study; thus, the time derivative with respect to porosity can be null (i.e. $\partial n/\partial t = 0$). It is worth to note that the effects of solution non-ideality, diffusion potential and semi-permeable membrane of compacted clays on the multi-ion diffusion were considered. Thus, the actual diffusion process of multiple ionic species can be characterized by the proposed model.

## 3 Model validation

### 3.1 Comparison with Barone's experimental results

Barone et al.[45] conducted laboratory model tests at a temperature of 10℃, in which the chemicals (i.e. $C1^-$, $Na^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$) of landfill leachate diffused through the saturated undisturbed clay. The numerical model with the same soil properties and boundary conditions was developed. Then, the simulation was conducted by the software COMSOL Multiphysics. As shown in Table 1, the diffusion coefficients of different ions at temperatures of 0 ℃ and 10 ℃ were estimated according to Li and Gregory[46]. The simulation results are compared with the experimental results of Barone et al.[45], as shown in Figs. 1 and 2. It can be seen that the modelling results agree well with the tests results by Barone et al.[45] regarding the variation of the concentration of $Na^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$ with respect to the diffusion depth.

**Table 1 Summary of parameters adopted for the validation of the model with results of Barone et al. [45]**

| Ionic species | | $Na^+$ | $K^+$ | $Cl^-$ | $Ca^{2+}$ | $Mg^{2+}$ |
|---|---|---|---|---|---|---|
| 0 ℃ | $D_1/(10^{-10}\ m^2/s)$ | 6.270 | 9.860 | 10.100 | 3.730 | 3.560 |
| 10 ℃ | $D_2/(10^{-10}\ m^2/s)$ | 8.151 | 12.818 | 13.300 | 4.849 | 4.628 |

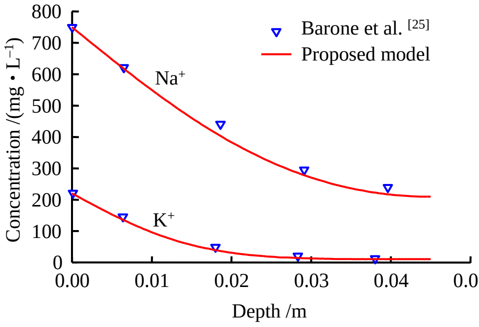

**Fig. 1 Comparison between computed and measured $Na^+$ and $K^+$ concentration**

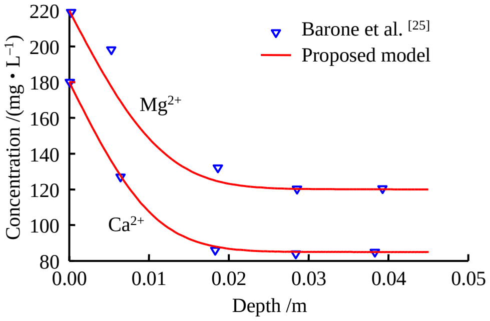

**Fig. 2 Comparison between computed and measured $Mg^{2+}$ and $Ca^{2+}$ concentration**

## 3.2 Comparison with Jungnickel's model

Jungnickel et al. [19] used the commercial code POLLUTE to simulate the multi-ion (i.e. NaF) diffusion process in saturated clay soils. To be consistent with Jungnickel's model, the non-ideality of the solution and semi-permeable membrane effect of clays were ignored in the proposed model. The simulation was conducted using the same boundary and initial conditions as those in Jungnickel's model. As shown in Figs. 3 and 4, the agreement with Jungnickel's model results validates the proposed model in this study.

# 4 Model applications

In this section, the proposed model was used to investigate the multi-ion diffusion process in clay barriers under combined actions. The influences of non-ideality in solution, diffusion potential and semi-permeable membrane effect of clayey soils on multi-ion diffusion were investigated.

## 4.1 Initial and boundary conditions

The initial and boundary conditions required for the simulation are given in Table 2.

In Table 2, $L$ is the thickness of the saturated porous media (i.e. clayey soil layer), $c_{i0}$ is the source concentration of ion species $i$（$i$=1, ⋯, $N$), $\lambda$ and $\mu$ are the parameters associated with the Cauchy boundary condition.

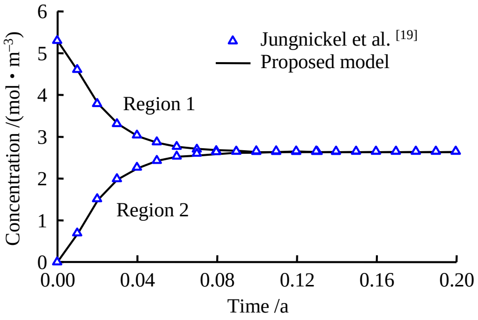

**Fig. 3 Comparison between computed and estimated (Jungnickel's model) variation of $Na^+$ and $F^-$ concentration with time**

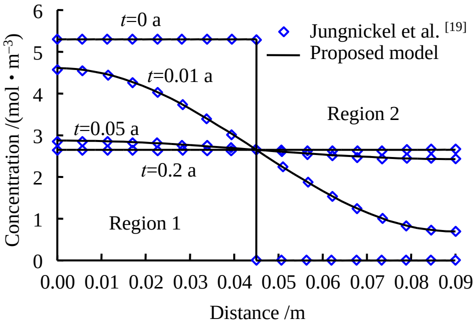

**Fig. 4 Comparison between computed and estimated (Jungnickel's model) variation of $Na^+$ and $F^-$ concentration with distance**

**Table 2 Initial and boundary conditions**

| Initial condition | $c_i(z,0)=0 \quad (0\leqslant z\leqslant L)$ |
|---|---|
| Upper boundary condition | $c_i(0,t)=c_{i0} \quad (t\geqslant 0)$ |
| Bottom boundary condition | $\lambda\dfrac{\partial c}{\partial z}+\mu c=0 \quad (t\geqslant 0)$ |

## 4.2 Model parameters

The source concentrations of ions were assumed to be constant. The chemical reactions among ions and those between ions in pore fluid and clay minerals were ignored. The parameters required for the numerical simulations are listed in Table 3.

**Table 3 Model parameters for simulating multi-ion diffusion process in a clay barrier**

| Parameters | Values | References |
|---|---|---|
| Clay barrier thickness, $L$ (m) | 2 | / |
| Tortuosity factor, $\tau$ | 0.6 | Li[47] |
| Initial boundary concentration (mol/L) | 0.1 | / |
| Osmotic efficiency coefficient, $\omega$ | 0.2 | / |
| Diffusion coefficient $Na^+$ ($m^2/s$) | $13.30\times10^{-10}$ | Shackelford and Daniel[3] |
| Diffusion coefficient $Zn^{2+}$ ($m^2/s$) | $7.02\times10^{-10}$ | Shackelford and Daniel[3] |
| Diffusion coefficient $Cr^{3+}$ ($m^2/s$) | $5.97\times10^{-10}$ | Shackelford and Daniel[3] |
| Diffusion coefficient $Cl^-$ ($m^2/s$) | $20.30\times10^{-10}$ | Shackelford and Daniel[3] |
| Boundary condition parameter $\lambda$ (m) | 17.37 | Wang et al.[48] |
| $\mu/\lambda$ | 50 | Zhang et al.[49] |

## 4.3 Simulation results and analysis

### 4.3.1 Influence of solution non-ideality on diffusion

To investigate the influence of solution non-ideality on ions diffusion, the effects of the diffusion potential and semi-permeable membrane effect of clay were ignored. Thus, the proposed model, i.e. Eq. (13) is simplified as below:

$$\gamma_i\frac{\partial(c_i)}{\partial t}+c_i\frac{\partial(\gamma_i)}{\partial t}+\nabla\tau\left[-D_i\left(\gamma_i\nabla c_i+c_i\nabla\gamma_i\right)\right]=0 \tag{14}$$

If the influence of solution non-ideality on ions diffusion is not considered (i.e. the activity coefficient $\gamma=1$), the proposed model, i.e. Eq. (13) degenerates to the general type including Fick’s first law as follows:

$$\frac{\partial c_i}{\partial t}+\nabla\tau\left(-D_i\nabla c_i\right)=0 \qquad (15)$$

The simplified models, i.e. Eq. (14) and Eq. (15) were used to conduct simulations on the multi-ion diffusion in the solutions of NaCl, $ZnCl_2$ and $CrCl_3$, respectively. The modelling results on the variation of the concentration of $Na^+$, $Zn^{2+}$ and $Cr^{3+}$ with the soil depth are shown in Figs. 5, 6 and 7. The evolution of ion concentration at the bottom boundary of the clay barrier with time is illustrated in Fig. 8. The simulations based on Eq. (14) and Eq. (15) correspond to results with and without considering solution non-ideality condition (NIC), respectively.

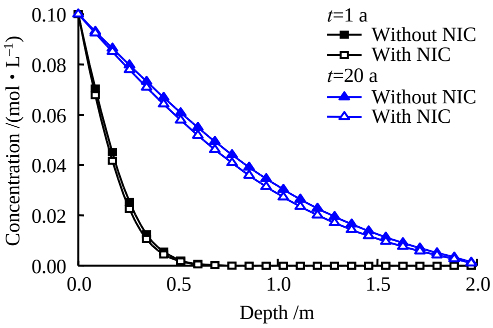

**Fig. 5 Distribution of $Na^+$ concentration with depth corresponding to 1 and 20 years. Comparison of results is made with and without considering NIC**

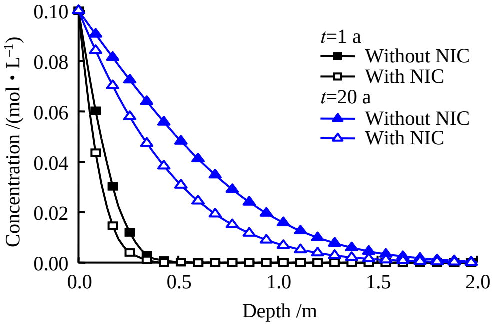

**Fig. 6 Distribution of $Zn^{2+}$ concentration with depth corresponding to 1 and 20 years. Comparison of results is made with and without considering NIC**

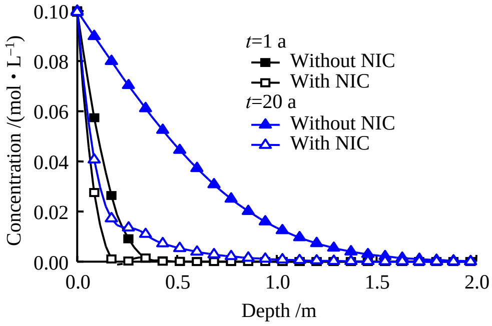

**Fig. 7 Distribution of $Cr^{3+}$ concentration with depth corresponding to 1 and 20 years. Comparison of results is made with and without considering NIC**

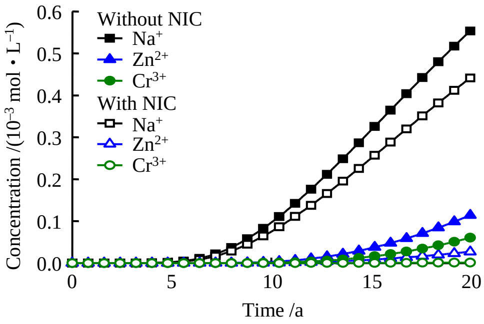

**Fig. 8 Distribution of concentration of various ions with diffusion time at the bottom boundary of a clay barrier**

It can be seen from Figs. 5, 6 and 7 that the ion concentrations have a declining tendency as the soil depth (i.e. diffusion distance) increases. In addition, the diffusion flux of ions considering the solution non-ideality is small than that ignoring the solution non-ideality. There are two mechanisms that contribute to this phenomenon. Firstly, the ion valence is a remarkable influencing factor regarding the diffusion flux through the clay barrier. As shown in Figs. 5, 6 and 7, the reduction in the diffusion flux becomes more remarkable with the increase of ion valence (i.e. $Na^+$, $Zn^{2+}$ and $Cr^{3+}$). In addition, the concentration difference due to NIC increases as the time elapses. When the ion valence is higher at a given soil depth, the ion concentration is lower. It indicates that the ion valence has a retarding effect on the ion diffusion. Secondly, solution non-ideality is another important factor which prolongs the ions diffusion. It can be seen from Figs. 5, 6 and 7 that at a given soil depth, the ion concentration with NIC is lower than that without NIC. Furthermore, the retarding effect on diffusion of NIC becomes more remarkable as time elapses.

Figure 8 illustrates the change in ion concentration with time at the bottom of the clayey soil layer. At a given diffusion time, it can be seen that the accumulated ion concentrations at the bottom without NIC are higher than those with NIC. It indicates that the non-ideality of solution due to the coexistence of multi-ions leads to a remarkable lagging effect on the ion diffusion. When the multiple ions mixed together, the electrostatic interactions among ions lead to solution non-ideality, which extensively modify the diffusion flux estimated by the ion concentration gradient (i.e. Fick’s first law). From the viewpoint of energy, the ions overcome the electrostatic force between ions to diffuse effectively. Additionally, the electrostatic force becomes stronger with the increase of ion valence, which reduces the diffusion driving force and consequently decreases the diffusion velocity.

### 4.3.2 Influence of diffusion potential on diffusion

To investigate the influence of diffusion potential due to electrostatic force between ions on the diffusion process, both the solution non-ideality and the semi-permeable membrane effect were ignored. Thus, the proposed model Eq. (13) can be simplified as

$$\frac{\partial c_i}{\partial t}+\nabla\tau\left(-D_i\nabla c_i+\frac{z_iD_ic_i}{\sum\limits_{j=1}^{N}z_j^2D_jc_j}\sum_{j=1}^{N}z_jD_j\nabla c_j\right)=0 \qquad (16)$$

The model in which the diffusion potential was considered, i.e. Eq. (16) was compared with the model that ignored the diffusion potential and estimated the diffusion flux using the Fick's first law, i.e. Eq. (15). Using the simplified models, Eq. (15) and Eq. (16), simulations were conducted on the multi-ion diffusion in the solutions of NaCl, $ZnCl_2$ and $CrCl_3$, respectively. The modelling results on the variation of the concentration of $Na^+$, $Zn^{2+}$ and $Cr^{3+}$ with soil depth are shown in Figs. 9, 10 and 11. The evolutions of ion concentration at the bottom boundary of clay barriers with time are shown in Fig. 12.

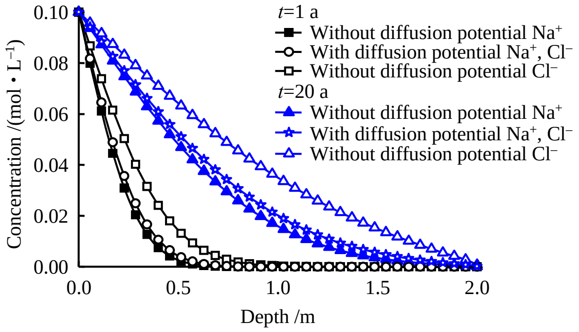

**Fig. 9 Distribution of $Na^+$ and $Cl^-$ concentration with depth in a clay barrier**

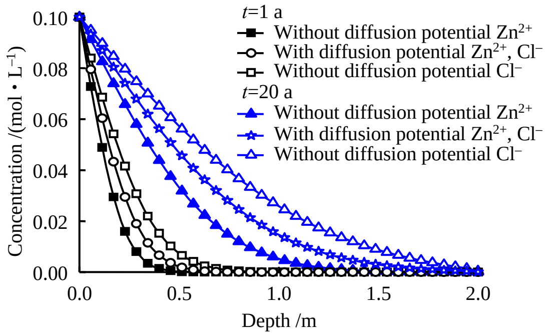

**Fig. 10 Distribution of $Zn^{2+}$ and $Cl^-$ concentration with depth in a clay barrier**

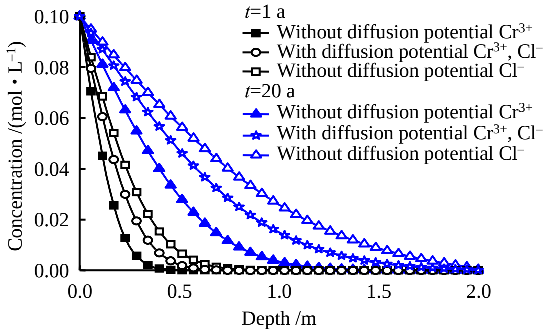

**Fig. 11 Distribution of $Cr^{3+}$ and $Cl^-$ concentration with depth of a clay barrier**

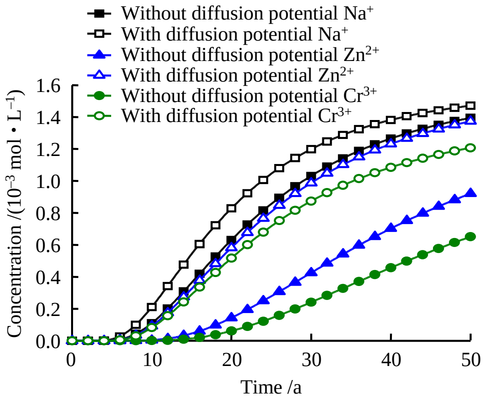

**Fig. 12 Distribution of concentration of various ions with diffusion time at the bottom boundary of a clay barrier**

As shown in Figs. 9, 10 and 11, the ion concentrations have a declining tendency as the soil depth (i.e. diffusion distance) increases. It can be seen that at a given soil depth, the ion with a higher valence has a lower concentration, which indicates a more remarkable influence of diffusion potential on diffusion process. However, the influencing mechanism of diffusion potential is different from that of solution non-ideality. When the diffusion potential is ignored in the model, the concentration values of cations are significantly lower than those of anions at a given soil depth. On the other hand, if the diffusion potential is considered in the model, the concentration of cation (e.g., $Na^+$) is equal to that of anion (e.g., $Cl^-$), which is between the simulated concentration of cation and that of anion excluding the effect of diffusion potential. The main reason is that the difference in diffusion flux of cations and anions will lead to an unbalance charge in solution. Therefore, the ion will be subjected to the action of surrounding ions and the electrical coupling between ions develops, which is called diffusion potential. The electrical coupling will slow down the faster ion and speed up the slower ion, such that the ions tend to cluster together to maintain the local and overall electroneutrality of solution. Because the diffusion velocities of cations ($Na^+$, $Zn^{2+}$ and $Cr^{3+}$) are lower than that of the anion ($Cl^-$), the diffusion potential will drive the cations to move faster and the anion to slow down. Finally, the concentration distribution of the cations and the anion coincide with each other, which is consistent with the pervious study by Ben-Yaakov[20].

Figure 12 illustrates the change in ion concentration with time at the bottom of the clayey soil layer. It can be seen that at a given diffusion time, the ion concentrations at the bottom considering the diffusion potential are higher than those ignoring the diffusion potential, which indicates that the diffusion process is strongly influenced by the diffusion potential. The electrical coupling accelerates the diffusion of cation, which leads to the accumulated concentration of cations ($Na^+$, $Zn^{2+}$ and $Cr^{3+}$) increase. The concentrations of cations considering the diffusion potential are different from those simulated by Fick's first law (i.e. Eq. (15)).

### 4.3.3 Influence of semi-permeable membrane on diffusion

To investigate the influence of the semi-permeable membrane effect of clay minerals on the diffusion process, both the solution non-ideality and diffusion potential were ignored. Thus, the proposed model is simplified as

$$\frac{\partial c_i}{\partial t}+\tau\left(1-\omega\right)\nabla\left(-D_i\nabla c_i\right)=0 \qquad (17)$$

The simulation results on the ion diffusion in the solution of $ZnCl_2$ by the simplified model, i.e. Eq. (17) that considered the semi-permeable membrane effect of clay were compared with those by the model which ignored the membrane effect, i.e. Eq. (15). In this study, the osmotic efficiency value was taken as 0, 0.2, 0.5 and 0.8 for the simulation using Eq. (17) taking the semi-permeable membrane effect of clay into consideration. When there exists the concentration difference across the clay liner, the water molecules are allowed to migrate through the liner. However, the migration of ions is influenced by the osmotic efficiency due to the semi-permeable membrane effect of clay. Thus, the water molecules in the solution with a lower ion concentration migrate through the clay liner, which dilutes the solution with a higher ion concentration. The osmotic efficiency $\omega$ has a remarkable influence on the simulation results on the diffusion of ions through the clay liner[50].

Figures. 13 and 14 show the variation of ion $Z_n^{2+}$ concentration with respect to the soil depth and the time, respectively. As shown in Fig. 13, the semi-permeable membrane effect of clay remarkably hinders the ion diffusion. Furthermore, as the osmotic efficiency increases, the ion concentration decreases gradually at a given soil depth. As shown in Fig. 14, at any diffusion time, the accumulated ion concentration at the bottom of the clay barrier without the semi-permeable membrane effect (i.e. $\omega$=0) is higher than that with the semi-permeable membrane effect (i.e. $\omega$>0). In addition, more remarkable is the semi-permeable membrane effect of clay (i.e., a greater value of $\omega$), more significantly the clay liner hinders the ion diffusion as shown in Figs. 13 and 14.

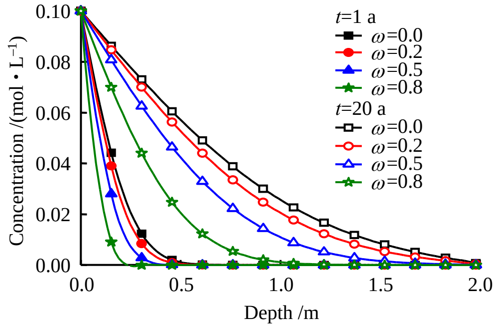

**Fig. 13 Distribution of $Zn^{2+}$ concentration with depth in a clay barrier**

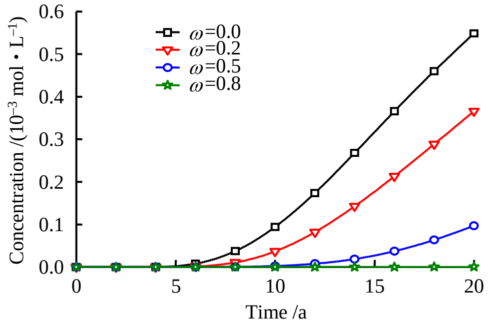

**Fig. 14 Distribution of $Zn^{2+}$ concentration with diffusion time at the bottom boundary of a clay barrier**

### 4.3.4 Influence of combined action on diffusion

Based on the above simulation results, it can be seen that the solution non-ideality, diffusion potential and semi-permeable membrane effect in clay significantly change the ion diffusion process, which should be considered in the prediction of solute transport or the design of landfill. In this subsection, $ZnCl_2$ was chosen as the contaminated source and the numerical simulation was conducted using the proposed model (i.e. Eq. (13)) considering the combined actions. To simulate the influence of the each factor mentioned above on the multi-ion diffusion, modelling results with models that consider each factor, i.e. Fick's model, model with NIC, model with diffusion potential, model with $\omega$=0.2 and model with combined actions are presented. Figure. 15 gives the variation of concentration of $Zn^{2+}$ with the soil layer depth when the diffusion time reaches 1 year and 20 years. Figure 16 indicates the variation of concentration of $Zn^{2+}$ with time at the bottom of the clay layer.

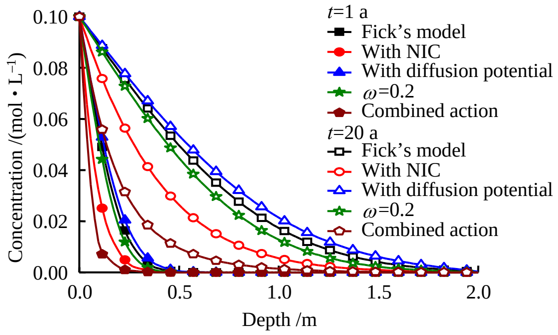

**Fig. 15 Distribution of $Zn^{2+}$ concentration with depth of a clay barrier**

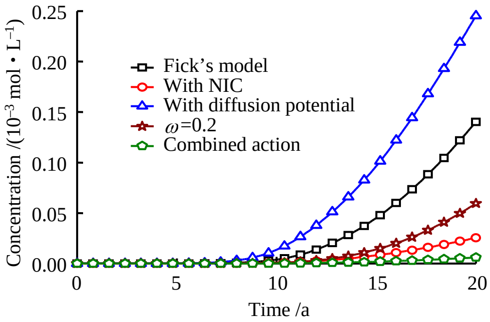

**Fig. 16 Distribution of $Zn^{2+}$ concentration with the diffusion time at the bottom boundary of a clay barrier**

The comparison between Fick’s model and models with each influencing factor have been discussed above, the influence of combined actions on the ion diffusion process will be investigated in detail. It is worth noting that the modelling results based on the proposed model have the lowest concentration at a given soil depth among the five models as shown in Fig. 15, which indicates that the combined actions has a most remarkable hindering effect on the ion diffusion. In addition, as shown in Fig. 16, the accumulated ion concentration calculated by the proposed model (i.e. Eq. (13)) has the smallest value among the five models at any given time at the bottom of the clay layer. Compared with Fick’s model, the influencing factors, i.e. solution non-ideality, semi-permeable membrane effect of clay and the combined actions have a retarding effect on the ion diffusion process. In contrast, the diffusion potential accelerates the diffusion of cations to maintain the local and overall electroneutrality. It should be noted that the simulation result based on the proposed model under combined actions (i.e. Eq. (13)) are the coupling effect not the simple superposition of the simplified models that consider each influencing factor. It can be concluded that the combined actions should be considered in the diffusion model when designing a landfill or estimating the solute transport in a saturated clay layer.

## 5 Conclusions

A multi-ion diffusion model through clay barriers under combined actions has been proposed. The influencing factors including solution non-ideality, diffusion potential and semi-permeable membrane effect of clay on multi-con diffusion process have been considered in this study. The proposed model has been validated by comparison between the modelling results and the previous experimental and numerical modelling results.

Numerical simulations have been conducted based on the proposed model using the software COMSOL Multiphysics. The following conclusions can be derived: (i) the diffusion potential has a promoting effect on the cation diffusion and a retarding effect on the anion diffusion; (ii) both the solution non-ideality and semi-permeable membrane effect of clay hinder the solute transport; and (iii) under the combined actions of influencing factors, the modelling results using the proposed model (Eq. (13)) have the lowest concentration compared with those using models that consider each factor, which indicates that the breakthrough time will be the longest under the combined actions. This study provides valuable information for the design of the clay liner of the landfill in engineering practice.

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