Multiphase modelling of ionic transport in cementitious materials with surface charges

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ABSTRACT

This paper presents a two-dimensional, two-phase ionic transport model with a surface charge at solid–liquid interfaces. The present model is applied to investigate the effect of surface charges at the solid–liquid interface on the ionic transport in a cement paste when it is subjected to an externally applied electric field. The surface charge in the present model is considered by modifying the Nernst–Planck equation in which the electrostatic potential is dependent not only on the externally applied electric field but also on the dissimilar diffusivity of different ionic species including the surface charges. The coupled transport equations of individual ionic species are solved numerically using a finite element method built in commercial software COMSOL. Some important features about the effect of surface charge on the concentration distribution, migration speed and flux of individual ionic species are discussed.

1. Introduction

Chloride induced corrosion of reinforcing steel in concrete has been recognized as the most critical threat to the durability of reinforced concrete structures, particularly those exposed to chloride-rich environment such as marine and offshore infrastructures [1]. It is generally acknowledged that reinforcing steel bars embedded in concrete start to depassivate when the concentration of the surrounding chloride reaches a certain threshold value [2–4]. The depassivation results in a significant corrosion rate of steel leading to cracking and spalling of the concrete cover, and eventually local failure of the structure. Therefore, it is important to understand how fast chloride ions can penetrate in the concrete, in order to predict the initial corrosion time and the service life of the structures in a given environment.

Since the early 1980s a considerable amount of laboratory and field tests have been carried out to investigate the mechanism of chloride ingress in concrete (e.g., [5–11]). These experimental methods can be classified into two categories. One is the diffusion test, in which the main driving force of the chloride penetration is the concentration gradient. The other is the migration test, in which the dominant driving force of the chloride penetration is the electrostatic potential gradient generated by the externally applied electric field. Based on the obtained experimental results, many prediction models have also been developed to examine the influence of various involved factors on the penetration of chloride ions in cementitious materials [12–26].

The diffusion and migration of ionic species in an electrolytic solution can be described by Fick’s Law and Nernst–Planck equation, respectively. In the early migration models developed for cementitious materials the electrostatic potential used in the Nernst–Planck equation is merely determined by the externally applied electric field. In this case, the transport equations of individual ionic species in the material can be treated separately and solved independently [5–8,27,28]. The influence of ionic interaction between different ionic species in cementitious materials on the electrostatic potential was considered first by Yu and Page [29], then Li and Page [15,16], and followed by others [24,30–36], in which the electrostatic potential is determined based on not only the externally applied electric field but also the internal electrostatic potential generated by the dissimilar diffusivity of different ionic species. Consequently, the transport equations of individual ionic species in the material are coupled each other and have to be solved dependently. Recently, the multicomponent transport model has been expanded from a single phase to two- and three-phases to consider the heterogeneous nature of the cementitious materials [20,37,38–40].
Despite the aforementioned numerous studies, there has been little work on the effect of the electrical double layer (EDL) on the ionic transport in cementitious materials. The EDL is a well-known electrochemical phenomenon, which can be found at the interface of the solid hydrates surface and the electrolytic pore solution in cementitious materials [41]. Due to the mixed mechanisms such as ionization, ionic adsorption and ionic dissolution, the cement hydrates will develop a surface charge when brought into contact with the pore solution [36]. The charge imbalance near the surface will create a local electric potential difference. Ions in the pore solution of opposite charge to that of the surface (countereions) are attracted towards the charged surface, while ions of like charge (coions) are repelled from the surface due to the electric force. However, of finite size, the centre of an ion can only approach the surface to within its hydrated radius without becoming specifically absorbed, which creates an inner layer called ‘stern layer’. Beyond the stern layer to the unaffected pore solution, the electric attraction and repulsion is combined by the mixing tendency resulting from the random thermal motion of the ions. These ions are then distributed in a ‘diffuse’ manner and this layer is called ‘diffuse layer’. The stern layer and diffuse layer form the structure of EDL [42]. The local electric charge and potential imbalance in the EDL have a great impact on ionic transport in porous media, especially in fine pores [43,44]. Therefore, the surface charge on the pore surface is another important factor that should be taken into account in the ionic transport in concrete.

In the past decade, much effort has been made to investigate the surface charge of various cement hydrate phases. Due to lack of direct test methods, most studies determined the sign and the magnitude of the surface charge in cementitious materials. Many researchers conducted zeta potential measurement on synthetic C–S–H suspensions [45–47], which are the main hydration products of cement-based materials. They found that the surface of C–S–H gel is negatively charged at low concentrations of Ca2+ in solution with a negative zeta potential. However, the zeta potential becomes positive when the concentration of Ca2+ is higher than a certain value. Elakneswaran et al. [48,49] studied the surface potential characteristics of different major mineral phases of hydrated cement paste. It was reported that Friedel’s salt and portlandite have positive surface charge while others show negative surface charge in water. Overall, the hydrated cement paste shows positive net surface charge by dissociation and adsorption. Nevertheless, the experimental results and theory of the surface charge are still not strong enough to make a general conclusion about the sign and the magnitude of the surface charge in cementitious materials.

Typically, the ionic and electric potential distributions in the EDL can be estimated by a linearized version of the Poisson–Boltzmann equation, which is only applicable at low potentials. With a constant electric potential boundary condition, one can get the results of electric potential distribution perpendicular to the charged surface, which is called the Debye–Hückel approximation. Then the ionic concentration distribution can be calculated by using the Boltzmann equation. However, the zeta potential measurements of cementitious materials indicate that the magnitude of the surface potential is relatively high for the linearization to be applicable [42]. Arnold et al. [50] presented a numerical solution of the full nonlinear Poisson–Boltzmann equations and examined the implications of EDL on the ionic diffusion in discrete pore geometries. The scheme is more applicable than the analytical Debye–Hückel approximation in cementitious materials. Friedmann et al. [51] developed an analytical solution of the Poisson–Boltzmann equation by replacing the Poisson equation with the electroneutrality approximation. They demonstrated that the overlapping of two diffuse layers in gel pores strongly influence the EDL effect on ionic transport. Nguyen and Amir [52] investigated the EDL effect on chloride penetration in unsaturated concrete by solving the multi-species ionic transport equations coupled with that of humidity. The EDL effect is introduced by modifying the chloride concentration with influencing parameters, which are mainly dependent on the zeta potential and the pore diameter. Their numerical results showed that the EDL effect reduces in unsaturated concrete due to the discontinuity of liquid phase, but increases in the concrete containing slag when compared to that with fly ash due to the high ionic strength of pore solution caused by the ferrous ions of slag.

In this paper, a two-dimensional numerical model is developed to simulate the transport of multiple species in a cement paste with surface charges. The model is used to simulate the ionic transport taking place in a cement paste when it is subjected to a rapid chloride migration (RCM) test. The numerical results show that there is an interaction between the local electric field generated by the surface charges and the global electric field generated by the externally applied voltage. The effect of surface charges at the pore surfaces on the ionic transport, particular the chloride penetration, in the two-dimensional model of cement paste is examined and discussed, through which the importance of using two-dimensional geometry is highlighted.

2. Two-dimensional, two-phase multicomponent ionic transport model with surface charges

It is assumed that the cement paste to be studied herein is fully saturated and there are no chemical reactions such as ionic adsorption/desorption between solid and liquid phases and ion–solvent molecules interactions in the pore solution. The transport of ionic species in the cement paste is the balance of the competing effects between the random thermal motion of the ions and the electric force, which is valid not only in the diffuse layer of EDL but also in the bulk solution where the effect of the surface charge can be ignored. The conventional Poisson–Boltzmann equation

<table>
<thead>
<tr>
<th>Notations</th>
<th>Description</th>
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<tbody>
<tr>
<td>$C_k$</td>
<td>concentration of k-th ionic species (mol/m$^3$)</td>
</tr>
<tr>
<td>$C_s$</td>
<td>surface charge at solid-liquid interfaces (mol/m$^3$)</td>
</tr>
<tr>
<td>$D_k$</td>
<td>diffusion coefficient of k-th ionic species (m$^2$/s)</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday constant (C/mol)</td>
</tr>
<tr>
<td>$J_k$</td>
<td>flux of k-th ionic species (mol/(m$^2$ s))</td>
</tr>
<tr>
<td>$N$</td>
<td>total number of ionic species in solution</td>
</tr>
<tr>
<td>$R$</td>
<td>universal gas constant (J/(mol K))</td>
</tr>
<tr>
<td>$t$</td>
<td>time (s)</td>
</tr>
<tr>
<td>$T$</td>
<td>absolute temperature (K)</td>
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<td>$x$</td>
<td>coordinate in horizontal axis (m)</td>
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<tr>
<td>$y$</td>
<td>coordinate in vertical axis (m)</td>
</tr>
<tr>
<td>$z_k$</td>
<td>valence number of k-th ionic species</td>
</tr>
<tr>
<td>$z_s$</td>
<td>valence number of surface charge</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>permittivity of a vacuum (C/(V m))</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>relative permittivity of water</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>electrostatic potential (V)</td>
</tr>
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</table>
incorporates both the thermal and electric effects to describe the influence of surface charges but is only applicable to one-dimensional problems, in which the local electrostatic potential generated by the EDL is not affected by the externally applied bulk electric field. For cementitious materials, however, the connective pores where ionic transport takes place are randomly distributed in the materials. When an external electric field is applied the bulk electric field is generally not perpendicular to the local electric field generated by the surface charge at randomly distributed pore surfaces. Therefore, the local and bulk electric fields may disturb each other. The interactive nature of these two electric fields may affect the transport of ions in the pore solution, the problem of which has not been addressed in the existing literature and is to be discussed here.

Here a cylindrical cement paste specimen used in the RCM test is considered. Because of the symmetry, the transport of ions in the specimen can be treated as a two-dimensional problem as shown in Fig. 1, where the cement paste is represented by a two-phase porous medium. The solid phase represents the solid part in the specimen where ionic transport cannot take place, whereas the liquid phase represents the transport medium where ionic transport can take place. The interface between the solid and liquid phases represents the pore surfaces where a surface charge exists. The specimen is exposed to NaCl and NaOH solutions on its left and right sides, respectively. The top and bottom sides of the specimen are sealed and therefore there is no ionic transport across these two boundaries. An external electric field is applied between the cathode placed in the NaCl solution and the anode placed in the NaOH solution as shown in Fig. 1.

The ionic flux of individual species in the liquid phase due to diffusion and migration can be expressed as follows,

\[
J_k = -D_k \nabla C_k - D_k \frac{z_k F C_k}{RT} \nabla \Phi \quad k = 1, 2, \ldots, N
\]  

where \( J_k \) is the flux, \( D_k \) is the diffusion coefficient, \( C_k \) is the concentration, \( z_k \) is the valence number, \( F = 96,480 \) C/mol is the Faraday constant, \( \Phi \) is the electrostatic potential, \( R = 8.314 \) J/(mol K) is the ideal gas constant, \( T = 298 \) K is the absolute temperature, subscript \( k \) stands for the \( k \)-th ionic species, and \( N \) is the total number of ionic species considered in the solution. The first and second terms in the right-hand-side of the equation represent the flux due to diffusion and migration, respectively. Note that the electrostatic potential in Eq. (1) is generated not only by the externally applied electric field but also by the dissimilar diffusivity of different ionic species involved in the solution including the surface charges. By using the conventional Poisson equation with considering the surface charges, the electrostatic potential in the solution domain can be determined as follows,

\[
\nabla^2 \Phi = -\frac{F}{\varepsilon_0 \varepsilon_r} \sum_{k=1}^{N} (z_k C_k + z_s C_s)
\]  

where \( \varepsilon_0 = 8.854 \times 10^{-12} \) C/(V m) is the permittivity of a vacuum, \( \varepsilon_r = 78.3 \) is the relative permittivity of water at temperature 25 °C, \( z_s \) and \( C_s \) are the valence number and concentration of the surface charge, respectively. Note that the surface charge exists only at the interfaces between solid and liquid phases and is taken as zero in the solution. The effect of the stern layer is not taken into account in this study for the sake of numerical simplicity. It is assumed that the thickness of stern layer is negligible compared to the size of the cement pores and the surface potential is equivalent to the zeta potential at the shear surface between the stern layer and diffuse layer [50].

The mass conservation of individual ionic species in a representative elementary volume in the liquid phase requires the following equation,

\[
\frac{\partial C_k}{\partial t} = -\nabla \cdot J_k \quad k = 1, 2, \ldots, N
\]  

where \( t \) is the time. Substituting Eq. (1) into (3), it yields,

\[
\frac{\partial C_k}{\partial t} = \nabla \left[ D_k \nabla C_k + D_k \frac{z_k F C_k}{RT} \nabla \Phi \right] \quad k = 1, 2, \ldots, N
\]  

Eqs. (4) and (2) are the governing equations applied to the liquid phase, which can be used to solve for the electrostatic potential \( \Phi \) and the concentrations \( C_k \) of individual ionic species if the initial and boundary conditions of \( \Phi \) and \( C_k \) are defined.

The above-described model is applied to simulate the ionic transport in the cement paste with pore surface charges when it is subjected to a RCM test. Note that, in RCM tests, the axially symmetric cross-section of the specimen is normally in the size of 50 × 50 mm (for a cylindrical specimen of diameter 100 mm and length 50 mm). However, the size of the EDL is much smaller, which is about tens nanometre to a few micrometre. In order to minimise the size effect a compromising solution domain of 5 × 5 mm is chosen (see Fig. 1), in which the solid and liquid phases are assumed to have an equal volume fraction, which represents a cement paste of water-to-cement ratio 0.54. Four ionic

<table>
<thead>
<tr>
<th>Variables</th>
<th>Chloride (mol/m³)</th>
<th>Hydroxide (mol/m³)</th>
<th>Potassium (mol/m³)</th>
<th>Sodium (mol/m³)</th>
<th>Voltage (V)</th>
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<tbody>
<tr>
<td>Initial conditions</td>
<td>( C = 0 )</td>
<td>( C = 400 )</td>
<td>( C = 300 )</td>
<td>( C = 100 )</td>
<td>( \Phi = 0 )</td>
</tr>
<tr>
<td>Boundary conditions at 0</td>
<td>( C = 400 )</td>
<td>( C = 0 )</td>
<td>( C = 0 )</td>
<td>( C = 400 )</td>
<td>( \Phi = 2.4 )</td>
</tr>
<tr>
<td>Boundary conditions at 5</td>
<td>( C = 0 )</td>
<td>( C = 400 )</td>
<td>( C = 0 )</td>
<td>( C = 400 )</td>
<td>( \Phi )</td>
</tr>
<tr>
<td>Boundary conditions at y = 0</td>
<td>( J = 0 )</td>
<td>( J = 0 )</td>
<td>( J = 0 )</td>
<td>( J = 0 )</td>
<td>( J = 0 )</td>
</tr>
<tr>
<td>Boundary conditions at y = 5</td>
<td>( J = 0 )</td>
<td>( J = 0 )</td>
<td>( J = 0 )</td>
<td>( J = 0 )</td>
<td>( J = 0 )</td>
</tr>
<tr>
<td>Valence number</td>
<td>( z = 0 )</td>
<td>( z = 1 )</td>
<td>( z = 0 )</td>
<td>( z = 0 )</td>
<td>( z = 1 )</td>
</tr>
<tr>
<td>Diffusion coefficient ( \times 10^{-11} ) m²/s</td>
<td>( D = 4.064 )</td>
<td>( D = 10.546 )</td>
<td>( D = 3.914 )</td>
<td>( D = 2.668 )</td>
<td>( )</td>
</tr>
</tbody>
</table>
species, namely potassium, sodium, chloride and hydroxyl are considered. The initial and boundary conditions of the four ionic species are given in Table 1. The externally applied voltage normally used in RCM tests is about 24 V, which produces a voltage gradient across the specimen of 48 V/cm. In order to make the solution domain have the same voltage gradient, the externally applied voltage employed in the present simulation is reduced to 2.4 V. The detailed boundary conditions of the electrostatic potential at four boundaries used in the simulation are also given in Table 1.

The surface charges on the interfaces between solid and liquid phases are assumed to be positive monovalent ions (i.e. $z_s = 1$) with a constant concentration of $C_s = 400\,\text{mol/m}^3$, which matches to the surface potential used in other studies, for example, [36,41,48,49].

The diffusion coefficients of the potassium, sodium, chloride and hydroxyl ions used in the present simulation are shown in Table 1, which are taken from corresponding values of them in dilute solution but divided by a factor of 50 to take into account the retardation that arises from the constriction and tortuosity of the pore path through which the ions are travelling.

Note that the ionic transport takes place in the liquid phase only. Hence, the finite element mesh is made also only in the liquid phase. The external boundary conditions described above are applied to the four sides ($x = 0$, $x = 5\,\text{mm}$, $y = 0$, $y = 5\,\text{mm}$). For the interface boundaries between the solid and liquid phases a zero flux boundary condition is used. To avoid the numerical difficulty caused by the sudden change in concentration of the charge from the interface to bulk solution, extremely small element sizes of about $10^{-7}\,\text{m}$ (see Fig. 2) are used in the regions near to the interfaces. In order to examine the effect of element sizes on the results, trials of different element sizes were conducted. The final mesh was chosen when the further reduction of element sizes has almost no effect on the obtained results.

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**Fig. 2.** Schematic of finite element mesh and surface charge.

**Fig. 3.** Chloride concentration profiles at four different times.
Fig. 4. Hydroxide concentration profiles at four different times.

Fig. 5. Potassium concentration profiles at four different times.
Fig. 6. Sodium concentration profiles at four different times.

Fig. 7. Comparison of average chloride concentrations.
3. Results and discussion

The governing Eqs. (2) and (4) with initial and boundary conditions defined in Table 1 are solved using the commercial software COMSOL. The details of the COMSOL software can be found in the COMSOL website and thus are not given further here. Instead, in what follows, only results and the discussion of the results are provided.

Figs. 3–6 show the concentration distribution profiles of the chloride, hydroxyl, potassium, and sodium ions in the liquid phase at four different times, in which the \( z \)-axis is the ionic concentration, the \( x \)- and \( y \)-axes represent the coordinate point \((x, y)\), respectively. These 3-D plots clearly illustrate the evolution of ionic transport with the time and the effect of the surface charges on the concentration distributions of the four ionic species, particularly in the regions near the charged surfaces. It can be seen from the figures that, under the action of the externally electric field applied between the two boundaries at \( x = 0 \) and \( x = 5 \) mm, the negatively charged ions (chloride and hydroxide) are forced to move from the cathode to the anode, while the positively charged ions (potassium and sodium) move from the anode to the cathode. In addition, due to the charge imbalance at the solid–liquid interfaces caused by the positive charge, the negatively or positively charged ions also move towards to or away from the charged surfaces while they are moving from one electrode to another. The electric attraction and repulsion, together with the effect of the concentration gradient, results in that the ionic distribution near the surface is in a 'diffuse' manner as mentioned before. However, the charge imbalance is highly localized and occurs only in very narrow regions close to the charged surfaces. As shown in Figs. 3–6, the concentrations of chloride and hydroxide increase steeply when approaching the solid–liquid interface, whereas the concentrations of potassium and sodium drop steeply. Note that the effect of the surface charge on the concentration distribution of individual ionic species is dependent not only on the amount of the surface charge but also on the ionic concentration in the bulk solution. The higher the concentration of an ionic species in the bulk solution, the larger the effect of the surface charge on the concentration distribution of that ionic species. The concentration increase of negatively charged ions or the concentration decrease of positively charged ions around the charged surface could be interpreted as the adsorption or desorption of ions due to the chemical attraction or repulsion of ions.

In order to investigate the overall effect of the surface charge on the transport of each ionic species along the \( x \)-axial direction, Figs. 7–10 provide the 2-D plots of individual ionic species for a quantitative comparison of ionic concentration distributions along the \( x \)-axis. Three average concentrations in \( y \)-axis are used in the figures. One is the average concentration in the liquid phase obtained with considering the effect of EDL; one is the average concentration in the liquid phase obtained without considering the effect of EDL; and one is the average concentration obtained in the 1-D and one-phase model (i.e. neither the solid phase nor the surface charge is considered in the model). It can be seen from Fig. 7 that, the transport of chloride ions slows down by a factor of about 1.5 when the solid phase is included in the model. This is probably due to the influence of tortuosity of the two-phase model. It is interesting to notice that, as far as the transport speed is concerned, the surface charge has almost no effect on the transport of chloride ions. However, in terms of the average
concentration, the positively charged surface leads to chloride to have marginally higher average concentration. The reason of this is probably due to the high chloride concentration along the charged surfaces but their layers are very thin.

The average concentrations shown in Fig. 8 for hydroxyl ions provide similar features. It is noted from the figure that the migration speed of the hydroxyl ions is almost the same as that of the chloride ions, although the diffusion coefficient of hydroxyl ions is about 2.5 times as that of chloride ions. This indicates that the interaction between different ionic species has a strong influence on the transport of individual ionic species. Figs. 9 and 10 show the average concentrations of potassium and sodium ions. It can be seen from the figures that, the transport speed of these two ionic species are also reduced when the solid phase is included in the model. However, unlike the negatively charged chloride and hydroxyl ions, the positively charged potassium and sodium ions have slightly lower average concentrations when the solid and liquid interfaces have a positive surface charge. In summary, it is found that the positive surface charge has more influence on the transport of negatively charged ions than that of the positively charge ions.

In the RCM test, the dominant ionic flux is the migration flux, which is proportional to the migration speed and ionic concentration as described in Eq. (1). Fig. 11 graphically shows the effects of the surface charge on the local ionic fluxes. The three ionic fluxes at the two points shown in the figure represent the fluxes induced by the diffusion, local electric field caused by the surface charge, and global electric field caused by the externally applied electric voltage, at a certain time. Of interest is the $x$-component of the chloride flux since it is primarily concerned in the test. There are three types of driven forces, which have contributions to the $x$-component of the chloride flux at a single point at the charged surface as well as in the diffuse layer near the charged surface. They are the concentration gradient, externally applied electric field along the $x$-axis, and the local charge imbalance caused by the surface charge, respectively. It can be seen from Fig. 11 that, the direction of the $x$-component of chloride flux resulting from the externally applied electric field along the $x$-axis remains the same across the whole domain. However, the direction of the $x$-component of chloride flux at the solid–liquid interface resulting from the concentration gradient and the surface charge is dependent on the normal direction of the charged surface. Thus, the $x$-component of the chloride flux will be influenced strongly by the pore geometry of the material. It is obvious that this feature cannot be explained by using the one-dimensional EDL model.

The main purpose of the RCM tests is to determine the diffusion coefficient of chloride ions in the tested specimen. There are two exercises that are currently used in the tests. One is to obtain the apparent diffusion coefficient [27] based on the depth, to which the chloride ions have penetrated in the specimen; the other is to obtain the effective diffusion coefficient [9] based on the flux of chloride ions, which has passed through the specimen. The former is controlled by the travel speed of chloride ions, whereas the latter is related to the flux of chloride ions, which is dependent on not only the speed but also the concentration of chloride ions. To examine the effect of the surface charge on the chloride flux, Figs. 12 and 13 show the comparison of $x$-components of chloride flux at two lines ($x = 1.25$ mm and $y = 1.3$ mm), obtained from the present simulation models with and without considering the surface charge. Note that, since the solid phase is discontinuous and
impermeable to ions the flux profiles plotted are not continuous in these figures.

It can be seen from Fig. 12a that, when the surface charge is not taken into account, the $x$-component of chloride flux at the line of $y = 1.3$ mm varies along $x$-axis. In general, the flux is lower at the place near to the solid surface and higher at the place far away from the solid surface, representing the obstacle effect of the solid phase on ionic transport in $x$-direction. In contrast, the $x$-component of chloride flux at the line of $x = 1.25$ mm shown in Fig. 13a also varies along $y$-axis, but it is dependent on the pattern of solid phase. In some regions the higher flux is found at the place near to the solid surface and the lower flux is at the place far away from the solid surface. While in other regions the flux increases/decreases from one solid surface to another solid surface, representing the effect of ahead and rear solid particles on ionic transport in liquid phase of the material when an externally applied electric field is involved.

When the surface charge is taken into account, however, the $x$-components of chloride flux at the two lines ($y = 1.3$ mm and $x = 1.25$ mm) are found to be quite different (see Figs. 12b and 13b) from those shown in Figs. 12a and 13a. Firstly, the surface charge significantly alters the $x$-component value of chloride flux in the region very close to a solid surface. Secondly, the scale value of the $x$-component of chloride flux close to a solid surface is about $10^{-3}$ mol/(m$^2$ s), which is about 10 times of that in the bulk solution. Thirdly, the effect of the surface charge on the $x$-component of chloride flux is only in very thin layer surrounding the solid surface as demonstrated in the zoom plots shown in Figs. 12b and 13b. Note that the effect of the surface charge on the $x$-component of chloride flux is different at the different points on the surface of a solid particle. For example, as is shown in Fig. 12b, the $x$-component of chloride flux reduces at the front point of a solid particle, but increases at the rear point of the solid particle. However, as is shown in Fig. 13b, the $x$-component of chloride flux could increase or decrease at the upper or lower point of a solid particle, depending on the pattern of the pore structure used in the model (i.e. the sizes and positions of its ahead and rear solid particles).
4. Conclusions

A 2-D, two-phase multicomponent ionic transport model has been developed in this paper. The present model has been applied to investigate the effect of surface charges at the solid–liquid interface on the ionic transport in a cement paste when it is subjected to an externally applied electric field. The surface charge in the present model is considered by modifying the Nernst–Planck equation in which the electrostatic potential is dependent not only on the externally applied electric field but also on the dissimilar diffusivity of different ionic species including the surface charges. The coupled transport equations of individual ionic species are solved numerically by using commercial software COMSOL. From the present study, the following conclusions can be drawn:

- The surface charge has a significant influence on the concentration distribution of ionic species but only in the region close to the charge surface. A positive surface charge increases the concentration of negatively charged ions but decreases the concentration of positively charged ions.
- The overall migration speed of ionic species in the two-phase model is found to be slower than that in the single-phase model because of the effect of tortuosity when the solid phase is involved. The surface charge at the solid–liquid interfaces seems to have very little influence on the overall migration speed of ionic species. This is mainly due to the layer of effect zone of EDL that is very thin when compared to its bulk solution zone.
- The surface charge has great influence on the chloride flux; but it is also only in the region close to the charge surface. A positive charge surface increases the $x$-component of chloride flux at the rear point of a solid particle, but decreases the $x$-component of chloride flux at the front point of a solid particle. A positive charge surface could increase or decrease the $x$-component of chloride flux at the upper or lower point of a solid particle, depending on the pattern of the solid and liquid phases used in the model.

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