



Movement of Contaminants through Kaolin Clay: A Numerical Approach

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ABSTRACT

Understanding the fate and movement of contaminants through soil is essential in applications such as ecological and environmental risk assessment. Abundance of clayey soil is available across the world. Presented in this paper is a parametric study of the movement of contaminants through clays. The current paper provides a holistic approach addressing these issues by providing an understanding of the factors influencing movement of contaminants in soil strata using available numerical models (advection and dispersion) for contaminant flow through porous medium. A numerical model using the finite difference and finite element method is considered in this study to estimate the contaminant transport phenomenon presented by Zhao *et al.* (1994) that utilises the analytical solution proposed by Ogata and Banks (1961). The results and discussions of the parametric study highlight the influence of various properties of soil and the contaminant on permeability and concentration (contaminant) variation with time and depth. The finding indicates that the diffusion coefficient (D_x) plays an important role in determining the time taken for the concentration of contaminants to be evenly spread in a vertical direction.

Keywords: Advection, clays, contaminant transport, dispersion, environment, permeability

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INTRODUCTION

Contamination is a cruel word to the environment; the condition exists in different phases: solid, liquid and gaseous. Movement of contaminants through the soil is one of the leading environmental concerns today. In recent years, interest in understanding the mechanisms and

prediction of contaminant transport through soils has radically increased because of growing evidence and public concern that the quality of the subsurface environment is being adversely affected by industrial, municipal and agricultural activities. Although contamination of groundwater system has a direct effect on the health of mankind, contamination of the porous medium, the soil strata itself, certainly presents a high environmental impact. This concern becomes urgent when the field conditions experience shallow water tables, thereby presenting a case of submerged soil deposits. Clays are a type of soil typically present in sites prone to contaminant effluents. Clays are also unique as they are commonly used as liners or barriers for waste landfill. Therefore, a thorough understanding of flow behaviour (permeability) and the change in mass flux of contaminants through these clayey deposits forms the essential assessment of contaminant transport and their influence. The main transport processes of concern in soil strata include advection, diffusion, dispersion, sorption and first-order decay (Shackelford, 1993). Advection is the movement of contaminants along with flowing ground water at the seepage velocity in porous media in response to a hydraulic gradient. Dispersion, on the other hand, is mass movement without bulk motion (Anderson, 1984). These important factors, addressed by Zhao, Xu and Valliappan (1994), present a review of numerical modelling on movement of contaminants through porous media.

However, the mass transport demonstrated that the flow due to advection is small in comparison to that due to dispersion.

A portion of the literature has since reviewed previous analytical and numerical solutions to predict the transport of contaminants through porous media subjected to time and depth (Zhao *et al.*, 1994; Rajasekaran, Murali, Nagan, Amoudhavally, & Santhaswaruban, 2005; Jaiswal, Kumar, & Yadav, 2011). Furthermore, insight into diffusion-related modelling studies is only now growing due to the limited availability of laboratory and field experimental data. In this paper, a contaminant transport model is presented for modelling of water infiltration and contaminant transport through the saturated soil zone. This paper highlights the variation of permeability of flow and change in concentration of the contaminant with time and depth. A numerical model using the finite difference and finite element method was considered in this study to estimate the contaminant transport phenomenon presented by Zhao *et al.* (1994) that utilised the analytical solution proposed by Ogata and Banks (1961). The permeability values in the current parametric study was estimated as a function of particle size, void ratio and viscosity of the contaminant using the homogenisation theory presented by Wang, Leung and Chow (2003). The materials considered for this study were clayey soils and methylene blue (MB). Although not strongly hazardous, MB can have various harmful effects such as nausea, vomiting,

diarrhea and chest pain, and this should be kept in mind when this substance is being used in laboratory work.

GOVERNING EQUATIONS

Soil formation processes are very complex and in reality, they display spatial variability in their geometric and hydraulic properties. Furthermore, due to lack of precise description of their structural irregularity from field and laboratory investigations, it is assumed in general engineering practice to be a homogeneous and isotropic medium. This assumption neglects small scale variations associated with heterogeneity and the averaged smooth flow of fluids through the porous medium. The numerical equation for advection and dispersion considered in this paper was presented by Zhao *et al.* (1994) and used the solution proposed by Ogata and Banks (1961). This equation assumes a homogeneous, isotropic and flow-saturated porous medium from the law of conservation of mass. Similarly, the equations used in this study to estimate the permeability of the soil medium was presented by Wang *et al.* (2003). The development part of this equation, discussed by Sriraam and Raghunandan (2014), are briefly addressed in this paper.

Advection-Dispersion Equation

The mass flux through a porous medium is derived from the mathematical statements of the conservation of mass. In a three-dimensional rectangular coordinate system, the specific discharge v

has three components including v_x , v_y and v_z . Therefore, the average linear velocity $v' = v/n$ also has three components v'_x , v'_y and v'_z where n is the porosity of the porous medium. The concentration of the contaminant solute as the mass of solute per unit volume of solution is expressed as C and mass of solute per unit volume of porous media is nC . On condition that the homogeneous medium of porosity is constant, the change in concentration gradient in x -direction is defined as $\partial(nC)/\partial x = n(\partial C/\partial x)$.

The mass of solute transported in x -direction by advection is represented by:

$$m_1 = v_x n C dA \quad [1]$$

and the mass of solute transported in x -direction by dispersion, derived from Fick's law is:

$$m_2 = n D_x \frac{\partial C}{\partial x} dA \quad [2]$$

The coefficients D_x and V_x are referred to as the solute dispersion coefficient and uniform velocity, respectively. Likewise, using the law of conservation of mass, the governing equation of mass transport through a porous medium can be derived as:

$$\frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z} = -n \frac{\partial C}{\partial t} \quad [3]$$

Equation (3) can be derived in a three-dimensional form and reduced to a one-dimensional form as:

$$D_x \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \quad [4]$$

Further, an analytical solution for this problem proposed by Ogata and Banks (1961) can be written as:

$$C(x, t) = \frac{C_0}{2} \left[\operatorname{erfc} \left(\frac{x - v_x t}{2D_x t} \right) + \exp \left(\frac{v_x x}{D_x} \right) \operatorname{erfc} \left(\frac{x + v_x t}{2D_x t} \right) \right] \quad [5]$$

where the solute concentration at position of the domain at time is given as t . The error function, erfc is the complementary error function and be expressed as:

$$\operatorname{erfc}(z) = \frac{2}{\sqrt{\pi}} \int_z^{\infty} \exp(-u^2) du \quad [6]$$

Fluid Flow in Porous Media

The flow equations, including seepage, presented by Wang *et al.* (2003), was derived from the Navier-Stokes equation using a low Reynolds number through a two-scale homogenisation method. A finite element technique further facilitated the derivation of the permeability coefficient. A micro-structural unit cell model was used to compute the flow and permeability values for a given void ratio. However, the expression used in this parametric study was limited to a one-dimensional unit cell that included two important parameters of equivalent particle size (d) and void ratio (e) in addition to the viscosity of the fluid (μ). Therefore, the coefficient of permeability was a function of these three parameters as shown below:

$$k = f(d, e, \mu) \quad [7]$$

The equivalent particle size (d) included a range of void ratios. However, the effect of a thin water film layer could not be eliminated completely. The adhesive water film around the particle generally formed a typical two-layer micro-structure. The water film therefore narrowed the flow

channels, thereby reducing the permeability of the porous media. However, the reduction ratio depended on pore size; the smaller the pore size, the larger the reduction ratio of the flow channels. Therefore, an effective void ratio was defined as the void ratio for free water passage between particles with adhesive water films where the thickness of water film was Δd , and the effective void ratio (e) was determined by:

$$e = \frac{d_1^0 - \Delta d}{d^0 + \Delta d} \quad [8]$$

and the equivalent particle size was

$$d_{\text{eff}} = d^0 + \Delta d \quad [9]$$

where the superscript ' 0 ' refers to the state without a water film $\Delta d \equiv 0$. A simple closed form solution was presented for the coefficient of the permeability in 1-dimensional flow as [7]:

$$k = \frac{\rho g}{\mu} \frac{(d_1^0 - \Delta d)^3}{d^0 - d_1^0} \quad [10]$$

where $(d^0 + d_1^0)$ was the characteristic size of a unit cell; hence when $d_1^0 - \Delta d \leq 0$, there was no flow passage and $k = 0$.

Model Parameters

The parameters governing the movement of contaminants through soils vary significantly depending upon the site specific conditions and perhaps the properties of the contaminant itself. Although the theory of parametric study is amenable to consider the entire spectrum of possible parametric combinations, the current study is limited to select parameters that are apparently more applicable to the

local conditions. However, to illustrate the significant factors arising from the use of the formulation presented above, the parametric study for the soil deposit considers a hypothetical case of 20m thick homogeneous clayey stratum with void ratio (e) varying between 0 and 3 (Shear *et al.*, 1992). In homogenised soil conditions with a free flow of contaminants, the particle size (d_{eff}) plays a crucial role in determining the void ratio. This is rather important as the higher the voids, the greater the increase in rate of contamination flow. Earlier studies on clays show an average d_{eff} of 0.002mm; hence d_{eff} throughout the current study is considered equal to 0.002mm. Another important parameter as evident from equation 2 is the thickness of the water film around the idealised individual soil particles. In general geotechnical practices, the thickness of the water film varies depending upon the geochemical interaction of the soil particles with the surrounding water molecules (Tripathy *et al.*, 2004), and is rather significant in the case of clays (Azam *et al.*, 2013; Khan *et al.*, 2014; Raghunandan *et al.*, 2014). However, a thickness of water film equal to 0.002mm was considered throughout this study.

Methylene Blue, $C_{16}H_{18}N_3SCl$, was selected as the contaminant for the current study. The density and viscosity of a contaminant plays a significant role as evidenced from equations 7-10. Therefore, the properties considered in this study were those of an aqueous solution (MB) with uniform concentration. The values

for the density and viscosity of MB used in this study were 1000kg/m^3 and 8.90mPa.s , respectively. The concentration gradient was a function of both space and time, critically influenced by advection, dispersion and flow velocity (Jaiswal *et al.*, 2011). The water table played a crucial role in aiding the mechanism of dispersion and advection, and the dispersion coefficient, D_x was the parameter that described the ability of a contaminant to disperse in water. The literature shows MB to have low D_x values of $0.3\text{--}0.6\text{m}^2/\text{day}$ through the water table (Boon *et al.*, 2003; Ferreira *et al.*, 2013). Therefore, a higher coefficient of dispersion should sharpen the boundary region for contaminant transport. In this study, the chemical reactions within the soil system were considered to be inert, pushing towards an idealised condition.

RESULTS AND DISCUSSION

Fig.1 shows the variation of permeability coefficient (k) of the contaminant model flow through soil strata with different void ratio (e) values. The flow parameter k is a function of the void ratio, where the size of the flow channels were perpendicular to the direction of flow, and the shape of the flow channels were parallel to the direction of flow. Higher values of e represent larger pores and vertical flow channels resulting in large k values. However, in the case of low e values, the pore volume reduces and tortuous flow channels further retard permeability through the soil strata.

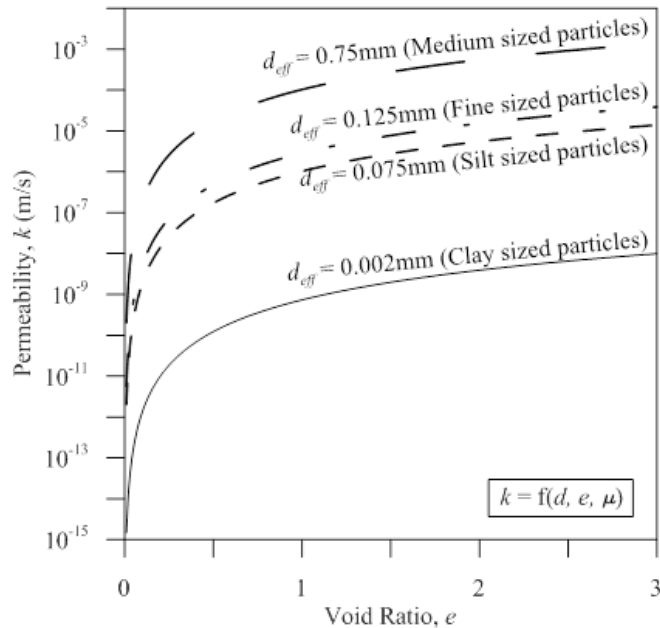


Fig.1: Variation of permeability of contaminant (MB) through the soil strata with varied void ratio.

The k values presented in the figure were explicitly calculated resulting in a vertical direction only. The parametric study presented here also considered different particle sizes expressed as d_{eff} in order to account for the change in soil type along the profile. However, the soil profile was considered to be homogeneous, which apparently formed one of the limitations of this study. The d_{eff} values selected included particle sizes that were equivalent to the soil sample such as clays (0.002mm), silts (0.075mm), fine sands (0.125mm) and medium sands (0.75mm). The model results, as anticipated, showed higher values of k with increasing d_{eff} . The increase in d_{eff} values certainly corresponded to an increase in e , thus producing clear and straight flow channels contributing to increased k values.

Referring to equation 7 used in this paper, the viscosity of the contaminant (μ) was identified as one of the significant contributors to evaluate permeability (k). Therefore, the parametric study would not be complete without studying the effect of μ on flow behaviour. Fig.2, thus, highlights the influence of the contaminant viscosity on flow behaviour. This is measured in terms of permeability of MB in a homogeneous deposit of clays. Observations from the figure show similar trends for the clay samples and the variation in the viscosity values sets an offset from the previous. For example, lower values of μ results in higher k values. Moreover, the variation pattern increases as the e values increase. This effect with increasing e values can be clearly explained considering the variation of k with e observed in Fig.1.

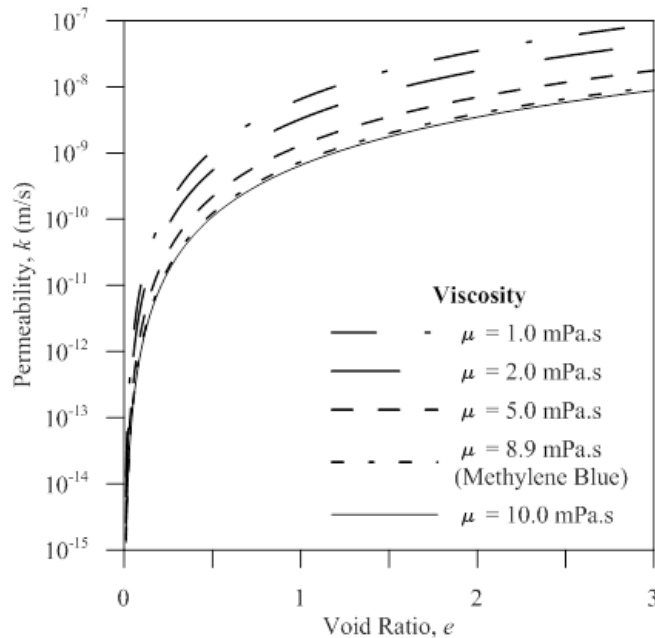


Fig.2: Influence of the void ratio of the clayey soil strata and the viscosity of the contaminant on the permeability coefficient of the contaminant.

In the previous discussion of Fig.1 it was clear the flow path and the e offered resistance to the fluid (contaminant) flow. Nonetheless, Fig.2 demonstrates a different perspective using another parameter μ having a significant role to play in dictating the fate of k for a given soil strata and fluid, that is, clay and MB in this study, respectively. The figure shows that the fluids with higher viscosity tended to take longer flow durations when studied at a particular depth of reference in the homogeneous soil strata.

Fig.3a - 3c show the variation of MB of relative concentration with depth at time durations of 24, 240 and 480 hours after the application of MB at the surface ($z=0$). The results were calculated for four different dispersion coefficients (D_x) at values 0.1, 0.2, 0.4 and 0.6 m^2/day .

The concentration of MB in this study was normalised with the initial concentration (C_0) and expressed as normalised concentration ratio (C/C_0). Increase in the value of D_x demonstrated an increase of concentration spread across the clayey strata at any depth over a defined time. As observed in the figure at any time t , the increasing value D_x results in lower concentration of the contaminant at a particular depth in the soil strata. In other words, a contaminant with a higher D_x value tends to disperse more compared to its movement in a vertical direction.

Further, the plots suggest that over a period of time, the concentration will tend towards its initial value ($C = C_0$). Therefore, the term D_x plays an important role in determining the time taken for a contaminant concentration to spread

evenly in the vertical direction. Similarly, Figures 4a – 4c show the variation of MB of relative concentration with time at depths 1, 10 and 20m from the ground surface ($z=0$). Observation of the figures shows that the concentration variation of the contaminant takes less time for the soil profile to be fully concentrated as compared with concentrations measured at a greater depth.

Observations clearly demonstrate that for the given dispersion coefficient, the C/C_0 reached its maximum at a lower

time duration; for example (from Fig.4a) the concentration reached 90% well under 500hrs at 1m depth, whereas the time taken for the contaminant to flow through 20m (from Fig.4c) initiated at around the 500th hour even at the high value of $D_x = 0.6 \text{ m}^2/\text{day}$. However, at time $t=1200\text{hrs}$ observed values from Fig.4c showed that only 5% of the concentration was achieved at depth 20m. This led to the conclusion that the rate of change of concentration reduces along the depth of soil layer.

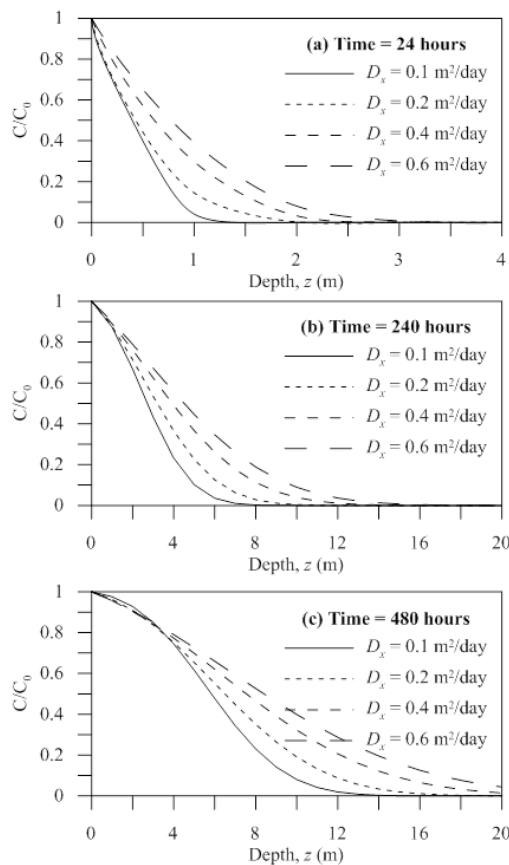


Fig.3: Effect of dispersion coefficient of MB on the concentration variation along the depth of clayey soil strata; (a) $t=24\text{hours}$, (b) $t=240\text{hours}$, (c) $t=480\text{hours}$.

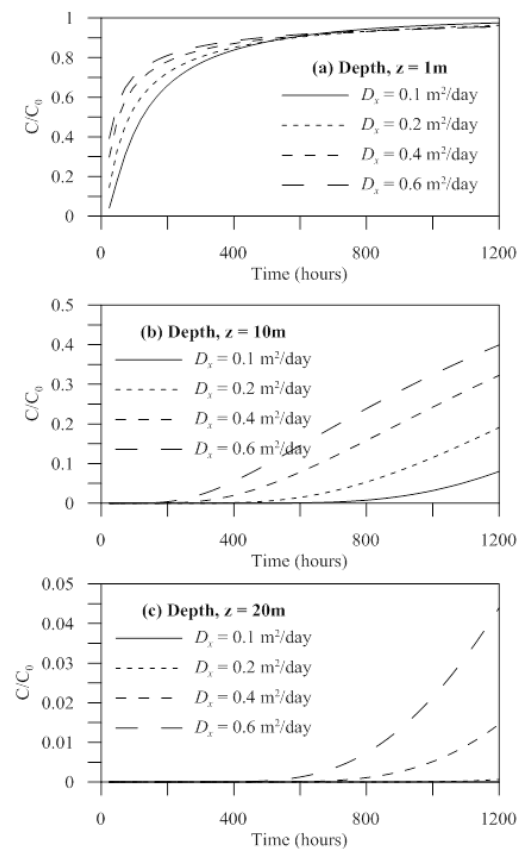


Fig.4: Effect of dispersion coefficient of Methylene Blue on the concentration variation with time after contamination application at the surface ($z=0$); (a) $z=1\text{m}$, (b) $z=10\text{m}$, (c) $z=20\text{m}$.

CONCLUSION

This paper highlights the influence of diffusivity and viscosity on permeability and movement of contaminants through clays. The numerical model was validated by application to a number of standard examples from the literature. This parametric study used numerical solutions on contaminant transport through porous media, giving importance to the advection and dispersion phenomena, methylene blue (contaminant) and clay (porous medium). The results and discussions further present the influence of the parameters on the permeability and concentration (contaminant) variation with time and depth of the idealised soil strata. To illustrate the effect of dispersion on concentration, a parametric analysis was performed on a range of dispersion coefficients from the available literature. Results from the numerical model estimated an increase in permeability with increasing d_{eff} . Since d_{eff} directly correlates to void ratio, a higher void ratio thus contributes to higher k values. The results also demonstrated that the higher viscous fluids tended to take longer flow durations when studied at a particular depth of reference in the homogeneous soil strata. Furthermore, the model to estimate the movement of contaminants suggested that over a period of time, the contaminant concentration will tend towards its initial value ($C = C_0$), therefore highlighting that the D_x value plays an important role in determining the time taken for the concentration of contaminants to be evenly spread in vertical direction.

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REFERENCES

- Anderson, M. P. (1984). Movement of contaminants in groundwater: Groundwater transport-advection and dispersion. *Groundwater Contamination*, 37-45.
- Azam, S., Shah, I., Raghunandan, M. E., & Ito, M. (2013). Study on swelling properties of an expansive soil deposit in Saskatchewan, Canada. *Bulletin of Engineering Geology and the Environment*, 72(1), 25-35.
- Boon, E. M., Barton, J. K., Bhagat, V., Nersissian, M., Wang, W., & Hill, M. G. (2003). Reduction of ferricyanide by methylene blue at a DNA-modified rotating-disk electrode. *Langmuir*, 19(22), 9255-9259.
- Ferreira, G. M. M., de Oliveira, F. M., Leite, F. R. F., Maroneze, C. M., Kubota, L. T., Damos, F. S., & Luz, R. D. C. S. (2013). DNA and graphene as a new efficient platform for entrapment of methylene blue (MB): Studies of the electrocatalytic oxidation of β -nicotinamide adenine dinucleotide. *Electrochimica Acta*, 111, 543-551.

- Jaiswal, D. K., Kumar, A., & Yadav, R. R. (2011). Analytical solution to the one-dimensional advection-diffusion equation with temporally dependent coefficients. *Journal of Water Resource and Protection*, 3(01), 76.
- Khan, F. S., Azam, S., Raghunandan, M. E., & Clark, R. (2014). Compressive strength of compacted clay-sand mixes. *Advances in Materials Science and Engineering*, 2014.
- Ogata, A., & Banks, R. B. (1961). *A solution of the differential equation of longitudinal dispersion in porous media: fluid movement in earth materials*: US Government Printing Office.
- Raghunandan, M. E., Sharma, J. S., & Pradhan, B. (2014). A review on the effect of rubber membrane in triaxial tests. *Arabian Journal of Geosciences*, 8(5), 3195-3206.
- Rajasekaran, G., Murali, K., Nagan, S., Amoudhavally, V., & Santhaswaruban, V. (2005). Contaminant transport modeling in marine clays. *Ocean engineering*, 32(2), 175-194.
- Shackelford, C. D. (1993). *Contaminant transport: Geotechnical practice for waste disposal* (pp. 33-65). Springer.
- Shear, D. L., Olsen, H. W., & Nelson, K. R. (1992). *Effects of desiccation on the hydraulic conductivity versus void ratio relationship for a natural clay*. Transportation research record, NRC, National academy press. Washington DC, 1993: 1365-1370.
- Sriraam, A., & Raghunandan, M. E. (2014). *Contaminant transport through peats: Soil behaviour and risk assessment*. Paper presented at the 7th International Conference on Environmental Geotechnics, Melbourne, Australia.
- Tripathy, S., Sridharan, A., & Schanz, T. (2004). Swelling pressures of compacted bentonites from diffuse double layer theory. *Canadian Geotechnical Journal*, 41(3), 437-450.
- Wang, J., Leung, C., & Chow, Y. (2003). Numerical solutions for flow in porous media. *International Journal for Numerical and Analytical Methods in Geomechanics*, 27(7), 565-583.
- Zhao, C., Xu, T., & Valliappan, S. (1994). Numerical modelling of mass transport problems in porous media: A review. *Computers & Structures*, 53(4), 849-860.