Journal of
Applied Sciences

Research Article
Diffusion of Chloride in Concrete under Fluctuating Environmental Conditions

[1]Chih-Hsing Wang and [2]Ching-Chang Lin

[1]Center for General Education, TransWorld University, 64043 Yunlin, Taiwan, Republic of China
[2]Department of Civil Engineering, Feng-Chia University, Taichung, Taiwan, Republic of China

Abstract

Background: This study investigated the one-dimensional diffusion of chloride under fluctuating environmental conditions to quantify the mass flux of a diffusing substance permeating a plate medium theoretically and verify it experimentally. **Materials and Methods:** An experiment was conducted by mounting a plate concrete specimen in the middle of a U-shaped tank, partitioning the tank into 2 halves. A solution involving fluctuating chloride concentrations was loaded on one side of the tank and fresh water was loaded on the other side. Chloride was predicted to permeate through the specimen. **Results:** The total amount of chloride diffusing through the specimen was monitored and fitted to the theoretical prediction. The diffusion coefficient, Neumann constant and proportional constant between the concentration of chloride in the environment and the corresponding saturated concentration of the concrete were quantified. **Conclusion:** The major contribution of this study is the use of Fick's diffusion law with the advancing model to accurately describe the permeation flux of a diffusing substance according to fluctuating concentrations of this substance in an environment. The parameters applied are critical in evaluating the service life of a reinforced concrete structure in a salty environment involving fluctuating concentrations of diffusing substances.

Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Studies on chloride diffusion in concrete are mostly based on Fick's diffusion law. Related tests include the Rapid Chloride Permeability Test (RCPT)[1,2], Accelerated Chloride Migration Test (ACMT)[3,4,5], ponding test[6] and immersion test[7]. The RCPT is most commonly used among these tests. Whiting developed the RCPT through electrochemistry and this test can be applied to rapidly evaluate the resistance of concrete against permeation by chloride in solution. Referring to the RCPT, Yang *et al*[3,5] developed the ACMT, which substantially reduced the disturbances from the generated heat and current induced by other negative ions except chloride. In the ponding test, concrete specimens are immersed in highly concentrated salty water. The diffusion coefficient of the chloride diffusing in concrete is calculated on the basis of the chloride permeation depth in the specimen. No electricity charge, which causes the decomposition of concrete is required.

The current study adopted the immersion test, which is based on a concept that is similar to the ponding test. In the immersion test, round concrete plate specimens are prepared. Each specimen is mounted between a U-shaped tank with salty water on one side and fresh water on the other side. The chloride concentration of the salty water must be maintained at a constant level by replacing the salty water weekly. On the other side of the tank, the chloride concentration of the water, which is fresh initially is measured and recorded weekly. After each measurement, the water is replaced by fresh water repeatedly[2]. Finally, the specimen is unloaded and tested for its diffusing substance concentration. The major contribution of this study is presenting an algorithm to characterize diffusion parameters under fluctuating environmental conditions.

MATERIALS AND METHODS

Fick's diffusion law[8]: In 1855, Fick proposed a mathematical law of diffusion for a scenario involving a substance diffusing in a medium. For one-dimensional (1D) diffusion, the law is:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \qquad (1)$$

where, D is the diffusion coefficient also called diffusivity, c is the concentration of the diffusing substance in the medium, defined as the mass of the diffusing substance in a unit volume of the medium, t is the diffusion duration and x is the coordinate in the diffusion direction.

Advancing diffusion model

Semi-infinite medium: Carslaw and Jaeger[9] have presented a solution for heat conduction in a semi-infinite medium by using the advancing boundary model. This mathematic model was used to derive the solution for 1D diffusion in a semi-infinite medium based on Fick's law[8]. When the diffusion begins at t = 0, the concentration of the diffusing substance in the medium is solved as:

$$c(t;x) = c_\infty \left[1 - \frac{\sum\limits_{m=0}^{\infty} \frac{(-1)^m \xi^{2m+1} v^{2m+1}}{m!(2m+1)}}{\sum\limits_{m=0}^{\infty} \frac{(-1)^m v^{2m+1}}{m!(2m+1)}} \right], \xi = \min\left(\frac{x}{2v\sqrt{Dt}}, 1\right) \quad (2)$$

In this case, the diffusing substance penetrates the surface of the medium and permeates toward its depth, where c_∞ is the saturation concentration of the diffusing substance in the medium, v is the Neumann constant and $2v\sqrt{Dt}$ is the permeation depth. The concentration of the diffusing substance of the external environment is constant. If the location is deeper than $2v\sqrt{Dt}$, then the concentration of the diffusing substance is zero, indicating that the location is uncontaminated.

Plate medium: Chang *et al*[10] and Wang *et al*[11] have presented solutions for the concentration of a diffusing substance in a plate medium according to Fick's law and the advancing model. In this study, the diffusing substance penetrates the surface on the left-hand side of a plate medium with a thickness of h and diffuses toward its surface on the right-hand side (Fig. 1). The concentration of the diffusing substance of the external environment in the left space is constant, whereas that of the substance in the right space is zero. When $t = t_p = h^2/(4v^2 D)$, the diffusing substance reaches the right surface. Before the diffusing substance reaches the right surface, the solution for the concentration of this substance in the medium is the same as Eq. 2. After the diffusing substance reaches the right surface, the solution becomes:

$$c(t;x) = c_\infty \left\{ 1 - \frac{x}{h} + 2\sum\limits_{n=1}^{\infty} \left[e^{-(\frac{n\pi}{h})^2 D(t-t_p)} \frac{\sum\limits_{m=1}^{\infty}\sum\limits_{r=1}^{m} \frac{(-1)^{n+m+r}(2m)! v^{2m+1}}{m!(2m+1-2r)!(n\pi)^{2r+1}}}{\sum\limits_{m=0}^{\infty} \frac{(-1)^m v^{2m+1}}{m!(2m+1)}} \sin\frac{n\pi x}{h} \right] \right\}$$

$$(3)$$

When $t > t_p = h^2/(4v^2 D)$, the diffusing substance starts to flow into the right space. The accumulated mass of the diffusing substance that permeates the plate medium to the right space is:
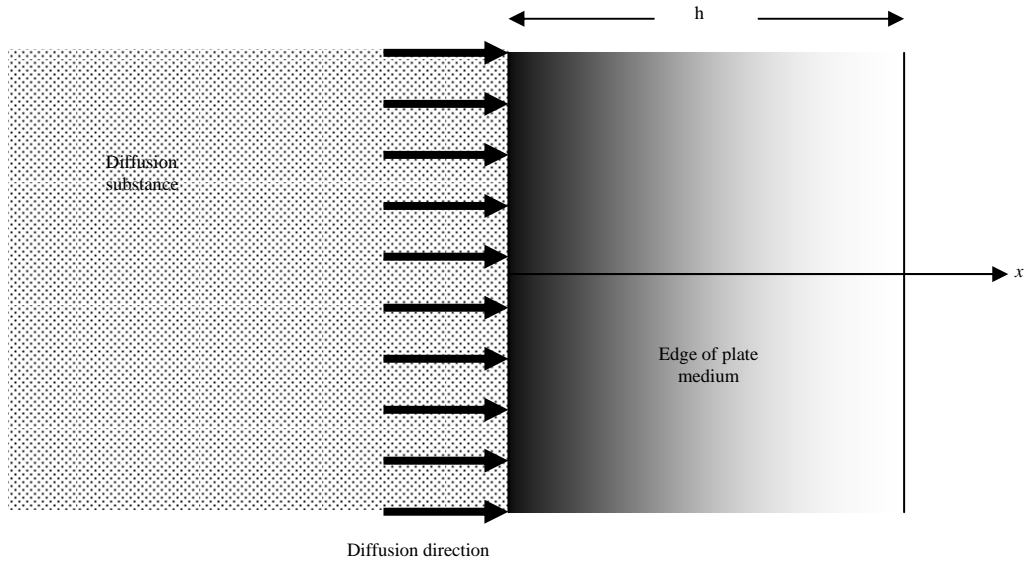
Fig. 1: Diffusion through a plate medium with thickness of h

$$M = AD\frac{c_\infty}{h}H(t-t_p)\left\{t-t_p - \frac{2h^2}{D}\frac{\sum_{n=1}^{\infty}\sum_{m=1}^{\infty}\sum_{r=1}^{m}\frac{[1-e^{-(\frac{n\pi}{h})^2 D(t-t_p)}](2m)!v^{2m+1}(-1)^{m+r}}{m!(2m+1-2r)!(n\pi)^{2(r+1)}}}{\sum_{m=0}^{\infty}\frac{(-1)^m v^{2m+1}}{m!(2m+1)}}\right\}$$

(4)

where, A is the cross-sectional area of the medium and H is the Heaviside unit step function and is defined as:

$$H(t-t_p) = \begin{cases} 0, & t-t_p \le 0 \\ 1, & t-t_p > 0 \end{cases}$$

(5)

Plate medium with fluctuating environmental conditions:
In the previous case, the diffusion begins at t = 0. If a diffusion process involves multiple stages that are initiated successively, then the diffusion in each stage corresponds to the concentration of the diffusing substance under the specified environmental condition, C. The ith diffusion stage starts at t = t_i instead of 0. Therefore, the lag must be removed from the process time to purify the diffusion duration. The corresponding accumulated mass induced by this stage should be:

$$M = \frac{AD}{h}c_{i\infty}H(t-t_i-t_p)\left\{t-t_i-t_p - \frac{2h^2}{D}\frac{\sum_{n=1}^{\infty}\sum_{m=1}^{\infty}\sum_{r=1}^{m}\frac{[1-e^{-(\frac{n\pi}{h})^2 D(t-t_i-t_p)}](2m)!v^{2m+1}(-1)^{m+r}}{m!(2m+1-2r)!(n\pi)^{2(r+1)}}}{\sum_{m=0}^{\infty}\frac{(-1)^m v^{2m+1}}{m!(2m+1)}}\right\}$$

(6)

where, $c_{i\infty}$ is the corresponding, c_∞ for the ith diffusion stage and Eq. 5 becomes:

$$H(t-t_i-t_p) = \begin{cases} 0, & t-t_i-t_p \le 0 \\ 1, & t-t_i-t_p > 0 \end{cases}$$

(7)

The total accumulated mass should be the summation of all the accumulated masses corresponding to each stage:

$$M = \frac{AD}{h}\sum_{i=1}^{I}\left\{\begin{array}{l} c_{i\infty}H(t-t_i-t_p)\{t-t_i-t_p \\ -\frac{2h^2}{D}\frac{\sum_{n=1}^{\infty}\sum_{m=1}^{\infty}\sum_{r=1}^{m}\frac{[1-e^{-(\frac{n\pi}{h})^2 D(t-t_i-t_p)}](2m)!v^{2m+1}(-1)^{m+r}}{m!(2m+1-2r)!(n\pi)^{2(r+1)}}}{\sum_{m=0}^{\infty}\frac{(-1)^m v^{2m+1}}{m!(2m+1)}}\} \end{array}\right\}$$

(8)

where, I is the number of stages. When $c_{i\infty}$ is assumed to be proportional to the concentration of the diffusing substance in the environment, $c_{i\infty} = k\Delta C_i$, where, ΔC_i is defined as the mass of the diffusing substance per unit volume of space in the environment for the ith stage and k is the proportional constant. Equation 8 becomes:

$$M = \frac{ADk}{h}\sum_{i=1}^{I}\left\{\begin{array}{l} \Delta C_i H(t-t_i-t_p)\{t-t_i-t_p \\ -\frac{2h^2}{D}\frac{\sum_{n=1}^{\infty}\sum_{m=1}^{\infty}\sum_{r=1}^{m}\frac{[1-e^{-(\frac{n\pi}{h})^2 D(t-t_i-t_p)}](2m)!v^{2m+1}(-1)^{m+r}}{m!(2m+1-2r)!(n\pi)^{2(r+1)}}}{\sum_{m=0}^{\infty}\frac{(-1)^m v^{2m+1}}{m!(2m+1)}}\} \end{array}\right\}$$
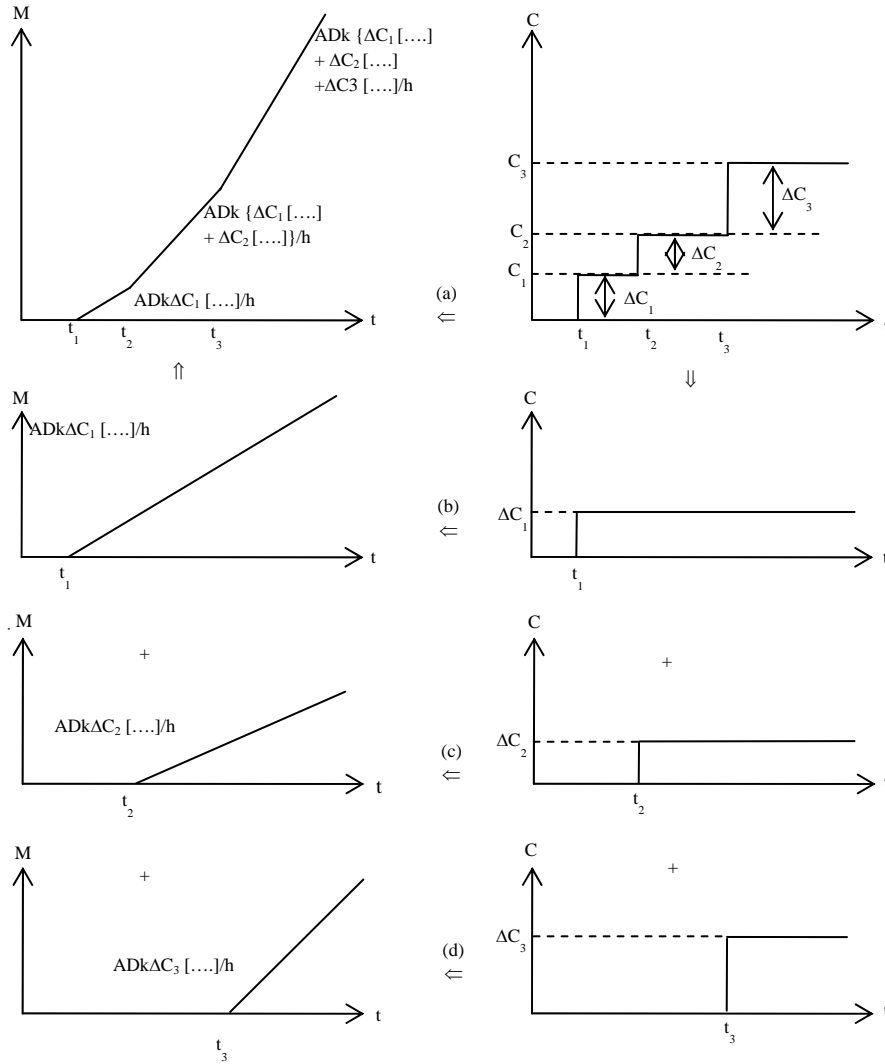
(9)

Fig. 2(a-d): Concentration of diffusing substance in the environment vs time and mass of diffusing substance penetrates the plate medium vs time for multi-stage diffusion containing each single-stage diffusion (a) Diffusion of multi-stage, (b) First stage of diffusion, (c) Second stage of diffusion and (d) Third stage of diffusion

In the studied case, the environmental condition of the left space illustrated in Fig. 1 fluctuates stage by stage and induces a change in $c_{i\infty}$. The concentration, C of a substance diffusing in an environment is defined as the mass per unit volume of solution surrounding the medium. Initially, the environment and the medium are free of the diffusing substance, $C = C_0 = 0$ and $c_\infty = c_{0\infty} = 0$, where C_0 and $c_{0\infty}$ are the initial C and c_∞, respectively. The first step of the diffusion process begins at $t = t_1$ and $C = C_1 = C_0 + \Delta C_1$ and the induced $c_\infty = c_{0\infty} + c_{1\infty} = kC_1 = k (C_0 + \Delta C_1)$ corresponds to C_1. The second step starts at $t = t_2$ and $C = C_2 = C_0 + \Delta C_1 + \Delta C_2$ and the induced $c_\infty = c_{0\infty} + c_{1\infty} + c_{2\infty} = kC_2 = k (C_0 + \Delta C_1 + \Delta C_2)$ corresponds to C_2. The third step begins at $t = t_3$ and $C = C_3 = C_0 + \Delta C_1 + \Delta C_2 + \Delta C_3$ and the induced $c_\infty = c_{0\infty} + c_{1\infty} + c_{2\infty} + c_{3\infty} = kC_3 = k (C_0 + \Delta C_1 + \Delta C_2 + \Delta C_3)$

corresponds to C_3 (Fig. 2). Therefore, in the first stage, $c_{1\infty} = k\Delta C_1$ is the change in c_∞ between the initial step and the first step in the second stage, $c_{2\infty} = k\Delta C_2$ is the change in c_∞ between the first step and the second step and in the third stage, $c_{3\infty} = k\Delta C_3$ is the change in c_∞ between the second step and the third step. About ΔC_1 is the change in C between the initial step and the first step, ΔC_2 is the change in C between the first step and the second step and ΔC_3 is the change in C between the second step and the third step.

This multistage diffusion process can be divided into several individual single-stage diffusion processes. The first single-stage diffusion involves a saturated concentration $c_{1\infty} = k\Delta C_1$, the second single-stage diffusion involves a saturated concentration $c_{2\infty} = k\Delta C_2$ and the third single-stage

diffusion involves a saturated concentration $c_{3\infty} = k\Delta C_3$. Combining all the single-stage diffusions yields the exact multistage diffusion involving fluctuating saturated concentrations, corresponding to an environment with fluctuating concentration conditions. For each single-stage diffusion process, the accumulated mass of the diffusing substance permeating the plate medium and then entering to the right space can be derived according to Eq. 6 and all single-stage diffusion processes can be combined, as shown in Eq. 8 and 9.

RESULTS

An immersion test involving fluness and 10 cm diameter were prepared and mounted individually between two PVC elbows with a 10 cm inner diameter (Fig. 3). The temperature of the environment was controlled to be $25\pm1°C$. Approximately 2000 cc of salt water was loaded in the left elbow and its top was sealed to prevent vaporization. The C level of the salt water in the left PVC elbow was set to change in a stepwise manner. In the first stage, $C = C_1 = 0.10$ g cm^{-3} for the first 35 days. In the second stage, $C = C_2 = 0.05$ g cm^{-3} for another 35 days. Finally, $C = C_3 = 0.01$ g cm^{-3} for the final 35 days. The salt water was replaced weekly to ensure that C remained constant. In addition, nearly 2000 cc of distilled fresh water was loaded in the right elbow and its top was sealed to prevent vaporization. This water was unloaded to be tested for its chloride concentration and replaced by fresh water weekly. To measure the concentration accurately, frequently condensing the water through vaporization to raise the concentration is necessary. In general, the water was condensed to approximately 1000 cc or even lower when the concentration was too low to be measured. Multiplying the

measured concentration by the water volume yields the chloride mass, which is the mass of chloride permeating the specimen.

The multistage diffusion process involves three individual single-stage diffusion processes: The first single-stage diffusion starts at $t = t_1 = 0$, $C = C_1 = 0.10$ g cm^{-3} and $c_{1\infty} = k (0.10-0.00) = k\,0.10$ g cm^{-3}; the second single-stage diffusion begins at $t = t_2 = 35$ days, $C_2 = 0.05$ g cm^{-3} and $c_{2\infty} = k (0.05-0.10) = -0.05$ kg cm^{-3} and the third single-stage diffusion starts at $t = t_3 = 70$ days, $C_3 = 0.01$ g cm^{-3} and $c_{3\infty} = k (0.01-0.05) = -0.04$ kg cm^{-3}. These 3 diffusion processes were combined to realize the multistage diffusion. The masses of chloride permeating the specimen to reach the right elbow were measured and accumulated weekly to obtain the total mass and the contaminated water was replaced by fresh distilled water. The four specimens were individually tested for 7, 14, 28, 35, 42, 49, 56 and 105 days. The accumulated masses of chloride permeating through the specimen into the right space were collected and fitted using Eq. 9 to obtain D, v and k (Fig. 4).

This experiment entailed simulating concrete material immersed in salt water. Moreover, 1D diffusion theory was applied to evaluate the unknown parameters, D, v and k in the theoretical formula from the results by using regression analysis.

In addition, the diffusion coefficient, Neumann constant and proportional coefficient between C and c_∞ were obtained by monitoring the mass flux of chloride penetrating the concrete specimen. When the chloride concentration in an environment fluctuates continuously, C depends on the diffusion duration and Eq. 9 becomes:
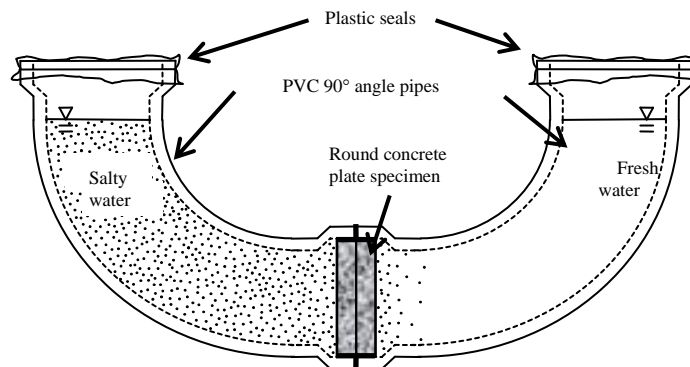

Fig. 3: A U-shape tank made of two PVC elbows with a round concrete plate specimen mounted at the middle to separate the tank into two halves, one with salty water on one side and the other with fresh water on the other side
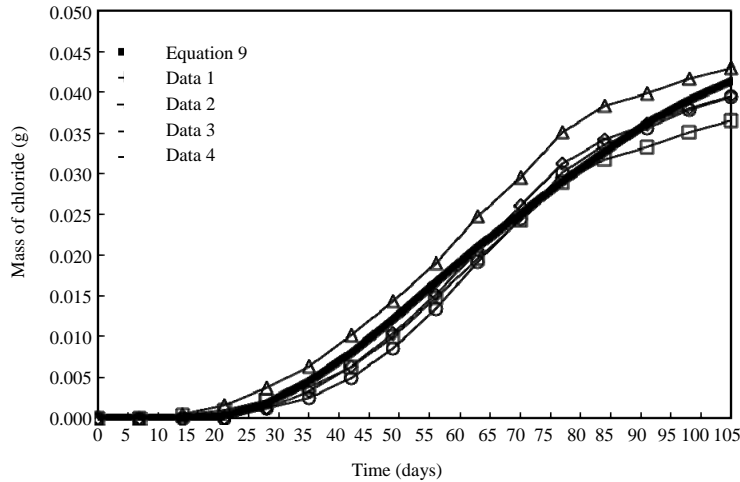
Fig. 4: Equation 9 with A = 78.54 cm², h = 2 cm, D = 1.606×10⁻² cm² day⁻¹, v = 1.873, k = 1.437×10⁻² and four sets of data of the total accumulated mass of chloride permeating through the concrete specimen into the night elbow

$$M = \frac{ADk}{h} \int_0^t \left\{ \begin{array}{l} C'H(t-\tau-t_p)\{t-\tau-t_p \\ \\ -\dfrac{2h^2}{D} \dfrac{\sum_{n=1}^{\infty}\sum_{m=1}^{\infty}\sum_{r=1}^{m} \dfrac{[1-e^{-(\frac{n\pi}{h})^2 D\,(t-\tau-t_p)}](2m)!v^{2m+1}(-1)^{m+r}}{m!(2m+1-2r)!(n\pi)^{2(r+1)}}}{\sum_{m=0}^{\infty} \dfrac{(-1)^m v^{2m+1}}{m!(2m+1)}} \end{array} \right\} d\tau$$

(10)

where, C is the derivative of C with respect to the diffusion duration τ. The parameters derived are used for quantifying the amount of chloride that permeates a concrete structure to reach a reinforcing bar at a certain depth of the structure and then induces corrosion after a certain duration. These parameters are critical for evaluating the service life of an RC structure.

As mentioned earlier, prior studies on chloride diffusion in concrete are mostly based on Fick's diffusion law. However, this study is presenting an algorithm to characterize diffusion parameters under fluctuating environmental conditions and the findings would provide a new study direction in relevant fields.

DISCUSSION

Diffusion parameters are generally obtained through a regression process according to a theoretical prediction from Fick's diffusion law and data[12-16]. However, the process of deriving diffusion parameters was modified in the current study. The test in this study involved simulating natural diffusion. No extra electricity charge was required, preventing

the generation of heat that severely affects the result and decomposes concrete however, this was at the expense of a long experimental period. Fluctuating chloride concentrations were applied in this study to simulate a marine environment for characterizing diffusion parameters this is the first diffusion parameter characterization approach in study on diffusion. An algorithm was developed for determining diffusion parameters under fluctuating concentration conditions in this immersion test and this algorithm was verified experimentally. The result was excellent and the derived parameters were applicable to predicting the service life of a Reinforced Concrete (RC) structure in marine environments.

CONCLUSION

This study investigated the one-dimensional diffusion of chloride under fluctuating environmental conditions to quantify the mass flux of a diffusing substance permeating a plate medium theoretically and verify it experimentally. The major contribution of this study is the use of Fick's diffusion law with the advancing model to accurately describe the permeation flux of a diffusing substance according to fluctuating concentrations of this substance in an environment. This is the first study to experimentally adapt fluctuating environmental conditions and the results were effectively fitted by a theory. The experiment entailed simulating a case of chloride diffusion in concrete immersed in salty water with fluctuating chloride concentrations, which occurs frequently in estuaries.

REFERENCES

1. AASHTO., 1996. Standard method of test for electrical indication of concrete ability to resist chloride ion penetration. American Association of State Highway and Transportation Officials, AASHTO T277-96, USA.
2. Whiting, D., 1981. Rapid measurement of the chloride permeability of concrete. Public Roads, 45: 101-112.
3. Yang, C.C., S.W. Cho, J.M. Chi and R. Huang, 2003. An electrochemical method for accelerated chloride migration test in cement-based materials. Mater. Chem. Phys., 77: 461-469.
4. Cho, S.W., C.C. Yang and R. Huang, 2002. Influence of aggregate content on the transport properties of mortar using accelerated chloride migration test. Concrete Sci. Eng., 4: 84-90.
5. Yang, C.C., S.W. Cho and R. Huang, 2002. The relationship between charge passed and the chloride-ion concentration in concrete using steady-state chloride migration test. Cement Concrete Res., 32: 217-222.
6. ASTM., 2005. Standard test method for determining the penetration of chloride ion into concrete by ponding. ASTM C1543-02, American Society for Testing and Materials, USA.
7. Chandran, D., H.K. Ng, H.L.N. Lau, S. Gan and Y.M. Choo, 2016. Investigation of the effects of palm biodiesel dissolved oxygen and conductivity on metal corrosion and elastomer degradation under novel immersion method. Applied Thermal Eng., 104: 294-308.
8. Crank, J., 1975. The Mathematics of Diffusion. 2nd Edn., Clarendon Press, Oxford, UK., ISBN-13: 9780198533443, Pages: 414.
9. Carslaw, H.S. and J.C. Jaeger, 1959. Conduction of Heat in Solid. 2nd Edn., Oxford University Press, London.
10. Chang, T.W., C.H. Wang and C.L. Tsai, 2008. Advancing boundary model for moisture diffusion in a composite laminate. J. Compos. Mater., 42: 957-973.
11. Wang, C.H., C.L. Tsai and C.C. Lin, 2011. Penetration lag of chloride diffusion through concrete plate based on advancing model. J. Mar. Sci. Technol., 19: 141-147.
12. Angilelli, K.G., J.R. Orives, H.C. da Silva, R.L. Coppo, I. Moreira and D. Borsato, 2015. Multicomponent diffusion during osmotic dehydration process in melon pieces: Influence of film coefficient. J. Food Process. Preserv., 39: 329-337.
13. Moon, J.H., M.J. Kim, D.H. Chung, C.H. Pan and W.B. Yoon, 2014. Drying Characteristics of sea cucumber (*Stichopus japonicas* Selenka) using far infrared radiation drying and hot air drying. J. Food Process. Preserv., 38: 1534-1546.
14. Horita, D., M. Yoshimoto, H. Todo and K. Sugibayashi, 2014. Analysis of hair follicle penetration of lidocaine and fluorescein isothiocyanate-dextran 4 kDa using hair follicle-plugging method. Drug Dev. Ind. Pharm., 40: 345-351.
15. Davie-Martin, C.L., K.J. Hageman and Y.P. Chin, 2013. An improved screening tool for predicting volatilization of pesticides applied to soils. Environ. Sci. Technol., 47: 868-876.
16. Doymaz, I., 2011. Drying of thyme (*Thymus vulgaris* L.) and selection of a suitable thin-layer drying model. J. Food Process. Preserv., 35: 458-465.