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# An Empirical Model to Predict Chloride Penetrations in Concrete Containing Palm Oil Fuel Ash Based on 10-Year Exposure Under Marine Environment

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## Abstract

The main objective of this study is to develop an empirical model for predicting the chloride penetration into concrete exposed to the sea water along shorelines. Concrete mixed with 0–50% of palm oil fuel ash, using W/B ratio of 0.40–0.50 were examined. Available database of concrete samples under the sea water submersion at 1, 3, 5, 7 and 10 years was collected. The study found that the developed empirical model could predict total chloride content in palm oil fuel ash concrete at any position below the concrete surface, which had been submerged under sea water for 1 year and over. The W/B ratio is also limited between 0.40 and 0.50. Application of this model is valid in the situation where penetration of chloride is in one direction. It was also shown that the margin of errors in this study is within  $\pm 35\%$  range when compared to the results presented by other researchers.

**Keywords** Empirical model, Chloride prediction, Chloride penetration, Palm oil fuel ash, Marine site

## 1 Introduction

An empirical model predicting durability of concrete structures under marine environment was developed in order to obtain optimal concrete mix design under expected service life. In this matter, concrete durability as well as economic aspect were taken into consideration. In addition, remaining reinforced concrete structures under marine environment can be assessed to determine damage conditions for further rehabilitations. Several research studies in the past have presented the development of mathematical models

for predicting deterioration of reinforced concrete structures (Kim et al., 2019; Chari et al., 2018; Alawi Al-Sodani et al., 2022; Farahani et al., 2015; Wang et al., 2019; Ju et al., 2021) and most of them were constructed using databases of chloride penetration that damaged reinforcing steel. Reinforced concrete structures under marine environment are subjected to wet and dry conditions repeatedly. Penetrating chloride would then accelerate the oxidation process in the reinforcing steel causing losses in load-resistant capability of concrete until failure (El-Khoury et al., 2022; Kiese et al., 2020; Kim et al., 2021; Otieno et al., 2016). Under such condition, damage protection due to chloride compounds should be the priority in a concrete mix design. Effectiveness and precision of the mathematical model were known to be predominantly influenced by the data used whether it corresponds to actual corrosion condition occurred under marine environment where reinforced concrete structures are subjected to physical and chemical impacts.

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Laboratory data often take less effort to obtain especially under controlled conditions; however, it does not solely reflect deteriorations of reinforced concrete structures under real marine environment that are complex in both physical and chemical natures (El-Khoury et al., 2022; Kiese et al., 2020).

Results from previous research (Chindapasirt et al., 2007) revealed that concrete containing palm oil fuel ash less than 35% by weight of binder, could reduce chloride penetration and water permeability coefficients in comparison to the conventional concrete. On the other hand, the mixture which contained palm oil fuel ash greater than 35% would increase both coefficients instead. Results also showed that percentage of chloride binding capacity increased when using palm oil fuel ash of less than 25% by weight (Chalee et al., 2021a). A further study on palm oil fuel ash concrete involved collection of data related to durability of concrete containing palm oil fuel ash placed along sea-shore for 7 years (Chalee et al., 2021a, 2021b). Results showed that the use of palm oil fuel ash in a replacement level of OPC of 15–35% by weight of binder, with a maximum W/B ratio of 0.45, can be used efficiently in concrete to enhance the service life of marine concrete structures. This is because palm oil fuel ash can activate the pozzolanic reaction very well with calcium hydroxide, the product of hydration reactions between the Portland cement and water (Al-Sabaei et al., 2022; Chalee et al., 2021a, 2021b; Hamada et al., 2018; Men et al., 2022). As a result, the compressive strength of concrete was increased, whereas its water permeability was decreased.

During the mix design process for preventing chloride penetration into concrete, database collected from samples submerged under the sea water is necessary. Long-term exposure period would realistically describe the real working conditions of concrete structures. Alternatively, available database of samples under true submersion was employed to predict the long-term penetration of chloride into concrete. The result from this study will be useful as a guideline for concrete to prevent or to reduce the chloride penetration over time. The maximum submerging period of 10 years is considered a long enough time that could represent the chloride penetration and deterioration of concrete in real nature. In addition, service life of reinforced concrete structures can also be predicted so that maintenance measures can be planned.

Therefore, the purpose of this study was to create an empirical model for predicting chloride penetration in conventional concrete (OPC concrete) and concrete containing palm oil fuel ash using a derived database of

chloride penetration in concrete under marine site for 1, 3, 5, 7 and 10 years.

## 2 Research Methodology

### 2.1 Binder and Aggregates

The binder used in this study was Portland cement type I. The Portland cement was partially replaced by palm oil fuel ash (P) that remained on a sieve No. 325 (45  $\mu\text{m}$  sieve) for less than 5% by weight. The palm oil fuel ash has a specific gravity of 2.33 and a median particle size of 10.1  $\mu\text{m}$ . The chemical compositions, approximately 69.7% of the palm oil fuel ash were  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . High amount of  $\text{SiO}_2$  (65.3%) was beneficial to the pozzolanic reaction. Chemical compositions of the binder materials are listed in Table 1. In this study, river sand was used as a fine aggregate with fineness modulus of 2.73 and a specific gravity of 2.73. The nominal maximum size of coarse aggregates was 19 mm.

### 2.2 Specimen Preparation and Testing

Concrete samples used in this study have W/B ratios of 0.40, 0.45, and 0.50. Type I Portland cement was partially replaced by palm oil fuel ash (P) at 0%, 15%, 25%, 35%, and 50% by weight of binder. The concrete slump test was conducted where the measured slump between 50 and 100 mm was targeted. In case that the measured slump falls out of the specified range, sulphonated melamine formaldehyde condensates (Supper P.) will be used as a water-reducer additive to enhance fresh concrete's workability. Concrete mix ingredients and compressive strength at 28 days are listed in Table 2. The concrete cubes  $200 \times 200 \times 200 \text{ mm}^3$  were casted. After 28-day water curing period, these concrete samples were submerged under the sea water at a test site along Chonburi Province's coastline, the gulf of Thailand. They were exposed to wet and dry conditions twice a day during

**Table 1** Chemical compositions of binder materials (Chalee et al., 2021a, 2021b)

Chemical composition (%)	Sample	
	Portland cement type I	Ground palm oil fuel ash (P)
Silicon dioxide, $\text{SiO}_2$	18.1	65.3
Aluminum oxide, $\text{Al}_2\text{O}_3$	5.5	2.5
Iron oxide, $\text{Fe}_2\text{O}_3$	3.2	1.9
Calcium oxide, CaO	64.9	6.4
Magnesium oxide, MgO	1.0	3.0
Sodium oxide, $\text{Na}_2\text{O}$	0.1	0.3
Potassium oxide, $\text{K}_2\text{O}$	0.5	5.7
Sulfur trioxide, $\text{SO}_3$	2.9	0.4
Loss on ignition, LOI	2.9	10.0

**Table 2** Mixture proportions of concrete used in this study (Chalee et al., 2021a, 2021b)

Mix	Mixture proportions of concretes (kg/m <sup>3</sup> )					W/B	Compressive strength at 28 days (MPa)
	Cement	Ground palm oil fuel ash (GPOFA)	Fine aggregate	Coarse aggregate	Water		
I40	480	0	765	935	190	0.40	48.3
I40P15	405	70	765	910	190	0.40	51.7
I40P25	360	120	765	895	190	0.40	48.0
I40P35	310	167	765	875	190	0.40	49.5
I40P50	240	240	765	850	190	0.40	44.6
I45	425	0	765	980	190	0.45	46.4
I45P15	360	65	765	955	190	0.45	48.4
I45P25	320	105	765	940	190	0.45	41.2
I45P35	275	150	765	925	190	0.45	40.3
I45P50	210	210	765	905	190	0.45	38.4
I50	385	0	765	1010	190	0.50	39.4
I50P15	330	60	765	990	190	0.50	37.6
I50P25	290	95	765	980	190	0.50	35.5
I50P35	250	135	765	965	190	0.50	36.0
I50P50	195	195	765	945	190	0.50	34.2

high tides and low tides. The sea water at the site has a pH range between 7.9 and 8.2, temperature ranged from about 25 to 35 °C. It has a chloride ion concentration between 16,000 and 19,000 mg/L, and sulphate concentration between 2200 and 2700 mg/L (Chalee et al., 2021a, 2021b).

After the concrete cubes had been exposed under the marine environment for 1, 3, 5, 7, and 10 years, each of them was drilled at the center and a core sample (5-cm diameter) was pulled out. Slices of core sample were cut off at different depths before being ground into fine particles. The sample particles at each depth level that passed through sieve No. 20 (850 µm sieve) were put to test for total chloride content measurement using acid-soluble chloride following ASTM C 1152. Fig. 1 illustrates sample preparations and chloride content measurements in the concrete.

### 3 Mathematical Modeling Techniques

A mathematical model was developed to predict total chloride concentration that penetrated into concrete containing palm oil fuel ash (P). The empirical model was based on 1, 3, 5, 7, and 10-year investigation of concrete exposed marine environment. Multiple regression analysis of data was carried out by applying Fick's second law of diffusion (Crank, 1975) as shown in Eq. 1:

$$\frac{\partial C}{\partial t} = D_c \frac{\partial^2 C}{\partial x^2} \quad (1)$$

In this equation, the chloride penetration coefficient ( $D_c$ ) had been widely accepted for its application towards



**Fig. 1** Specimen preparations and chloride content measurements in the concrete

on-site testing where concrete samples were exposed under marine environment (Thomas & Matthews, 2004). Previous study (Chalee & Jaturapitakkul, 2009) concluded that the chloride penetration coefficient gradually decreased as the exposure time increase; hence, the coefficient ( $D_c$ ) in Eq. 1 should be adjusted accordingly. A research study by Mangat and Limbachiya (Mangat & Limbachiya, 1999) proposed a relationship between the coefficient ( $D_c$ ) and exposure time of concrete exposed to surrounding chloride as shown in Eq. 2:

$$D_c = (t)^{-k_1} \tag{2}$$

Substituting  $D_c$  value from Eq. 2 into Eq. 1 result will show in Eq. 3:

$$\frac{\partial C}{\partial t} = t^{-k_1} \frac{\partial C^2}{\partial x^2} \tag{3}$$

General solution of Eq. 3 is carried out in Eq. 4:

$$C_{x,t} = C_0 \left[ 1 - \operatorname{erf} \left( \frac{x}{\sqrt{\frac{2t(1-k_1)}{1-k_1}}} \right) \right] \tag{4}$$

Equation 4 quantifies the chloride content ( $C_{x,t}$ ) that penetrates into concrete at the distance  $x$  below concrete surface and exposure time between concrete and surrounding chloride ( $t$ ). It is noted that the unit of time ( $t$ ) has been changed from seconds in Eq. 4 into years in Eq. 5:

$$C_{x,t} = C_0 \left[ 1 - \operatorname{erf} \left( \frac{x}{\sqrt{\frac{2 \cdot 31536000 t^{(1-k_1)}}{1-k_1}}} \right) \right], \tag{5}$$

where  $C_{x,t}$ =chloride content (% by weight of binder) at distance  $x$  from below surface and the exposure time between concrete and surrounding chloride ( $t$ );  $t$ =exposure time (years);  $x$ =distance below concrete surface (mm);  $C_0$ =chloride content (% by weight of binder) at concrete surface ( $x=0$ ) at exposure time  $t$ ;  $k_1$ =coefficient; erf=error function which is

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-n^2} = \frac{2}{\sqrt{\pi}} \sum_{n=1}^{\infty} \frac{(-1)^n z^{(2n+1)}}{n!(2n+1)}$$

$$= \frac{2}{\sqrt{\pi}} \left( z - \frac{z^3}{3} + \frac{z^5}{10} - \frac{z^7}{42} + \dots \right)$$

To determine chloride penetration in Eq. 5, it is necessary to obtain the value of coefficient  $k_1$  and chloride concentration on the concrete surface ( $C_0$ ). The regression analysis of Eq. 5 uses chloride penetration from concrete samples that has been submerged under the sea water up to 10 years. Fig. 2 describes the calculation details for the values of  $k_1$  and  $C_0$  of concrete with W/B of 0.45, by way of regression analysis using adjusted

values of  $k_1$  and  $C_0$  from Eq. 5. These values were adjusted in such a way that this graph corresponded to the chloride penetration data of all the concretes mixed with palm oil ash at different ages exposed to sea water. The empirical coefficient  $k_1$  and  $C_0$  of all concrete mixtures are shown in Table 3.

The value of  $k_1$  in Table 3, it has no obvious trend with respect to W/B ratio; however, there was a relationship for concretes which are substituted Portland cement with palm oil fuel ash and exposure time. The average value of  $k_1$  of the concrete mixed with ground palm oil fuel ash with various exposure times is shown in Table 4. Fig. 3 shows the regression analysis based on Table 4, between  $k_1$  and exposure time ( $t$ ), which gives the relationship as shown in Eq. 6:

$$k_1 = [k_2 \ k_3] \begin{bmatrix} \ln(t) \\ 1 \end{bmatrix} \tag{6}$$

The regression analysis between  $k_2$  and  $k_3$  values and ground palm oil fuel ash content ( $P$ ) as shown in Fig. 4, the relationship can be obtained as in Eq. 7:

$$\begin{bmatrix} k_2 \\ k_3 \end{bmatrix} = \begin{bmatrix} 0.00 & -0.0002 & -0.0334 \\ -6(10)^{-5} & 0.0043 & 0.7793 \end{bmatrix} \begin{bmatrix} P^2 \\ P \\ 1 \end{bmatrix} \tag{7}$$

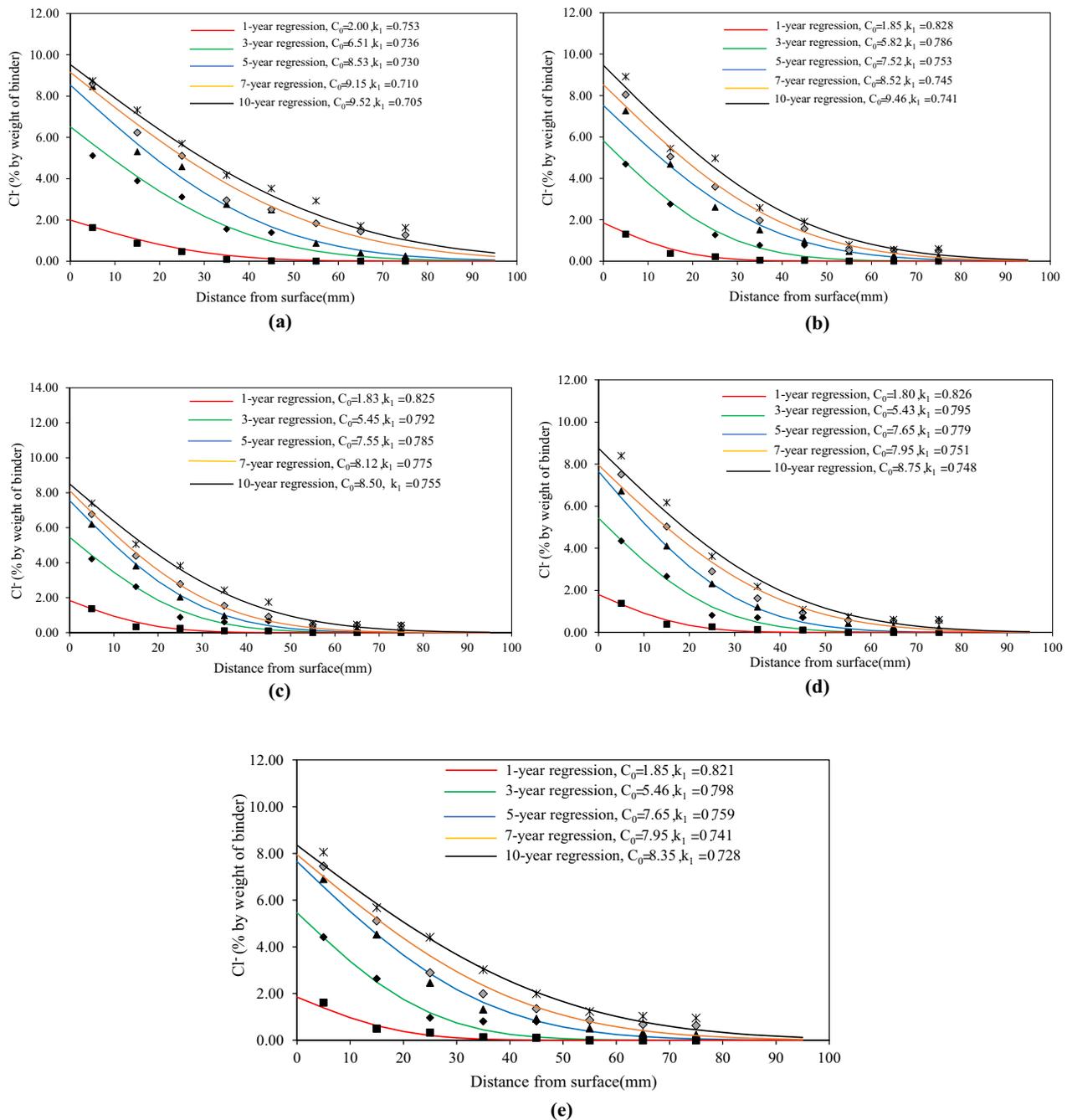
where  $k_1$ ,  $k_2$ , and  $k_3$ =the empirical coefficients;  $P$ =percentage of Portland cement type I replaced by ground palm oil fuel ash; Using Eqs. 6 and 7, the value of  $k_1$  can be expressed in terms of substituting ground palm oil fuel ash ( $P$ ) and exposure time ( $t$ ).

The value of  $C_0$  has no relationship with ground palm oil fuel ash content; however, there was an ascending trend with respect to submerging time of concrete samples under sea water environment. During mathematical modeling process, an average value of  $C_0$  at each W/B ratio was selected in the regression analysis with the submerging time of concrete samples. The relationship between  $C_0$  and the submerging time ( $t$ ) as shown in Fig. 5, can be expressed in a logarithmic function as stated in Eq. 8:

$$C_0 = [k_4 \ k_5] \begin{bmatrix} \ln(t) \\ 1 \end{bmatrix} \tag{8}$$

Regression analysis on the relationship between the  $k_4$ ,  $k_5$  coefficient and the W/B ratio according to Fig. 6, yields the relationship in Eq. 9:

$$\begin{bmatrix} k_4 \\ k_5 \end{bmatrix} = \begin{bmatrix} 7.628 & -0.1196 \\ 6.589 & -0.8411 \end{bmatrix} \begin{bmatrix} W/B \\ 1 \end{bmatrix} \tag{9}$$



**Fig. 2** Regression analysis to determine  $C_0$  and  $k_1$  values in palm oil fuel ash concrete with a W/B ratio of 0.45. **a** Portland cement type I concrete. **b** 15% palm oil fuel ash concrete. **c** 25% palm oil fuel ash concrete. **d** 35% palm oil fuel ash concrete. **e** 50% palm oil fuel ash concrete

Equations 8 and 9 reveal that the value of  $C_0$  can be evaluated in terms of W/B ratio and exposure time ( $t$ ). The values of  $k_1$  and  $C_0$  can be used to calculate chloride content (% by weight of binder) at distance  $x$  below the concrete surface and submerging time under the chloride environment ( $t$ ) from Eq. 5.

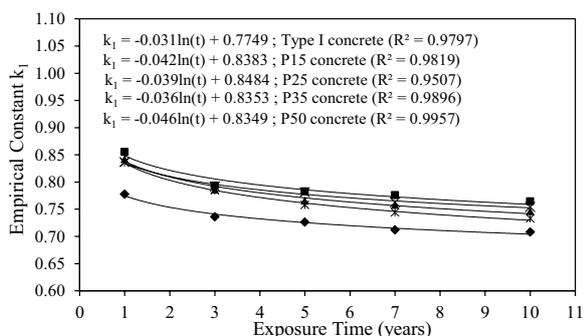
The established model can predict total chloride content at any depth from the concrete surface with respect to exposure time beyond 1 year. It is under some assumptions that the substituting of Portland cement type I by ground palm oil fuel ash does not exceed 50% and W/B ratios are among 0.40–0.50. However, the empirical model is valid only for uncracked reinforced concrete

**Table 3** The empirical coefficient  $k_1$  and chloride concentration at concrete surface ( $C_0$ )

Mix	Empirical coefficients $k_1$					Chloride concentration at concrete surface, $C_0$ (% by weight of binder)				
	1 year	3 years	5 years	7 years	10 years	1 year	3 years	5 years	7 years	10 years
I40P00	0.825	0.738	0.725	0.721	0.728	1.80	5.95	7.15	7.45	8.95
I40P15	0.875	0.789	0.785	0.782	0.772	1.45	5.65	7.25	8.15	8.95
I40P25	0.876	0.799	0.798	0.795	0.793	1.43	5.15	6.55	7.65	8.25
I40P35	0.879	0.795	0.782	0.775	0.765	1.40	6.15	6.75	7.35	7.95
I40P50	0.876	0.769	0.755	0.75	0.743	1.43	5.15	6.15	6.95	8.55
I45P00	0.753	0.736	0.730	0.71	0.705	2.00	6.51	8.53	9.15	9.52
I45P15	0.828	0.786	0.753	0.745	0.741	1.85	5.82	7.52	8.52	9.46
I45P25	0.825	0.792	0.785	0.775	0.755	1.83	5.45	7.55	8.12	8.50
I45P35	0.826	0.795	0.779	0.751	0.748	1.80	5.43	7.65	7.95	8.75
I45P50	0.821	0.798	0.759	0.741	0.728	1.85	5.46	7.65	7.95	8.35
I50P00	0.755	0.734	0.725	0.705	0.692	2.51	6.52	10.51	11.50	11.90
I50P15	0.825	0.784	0.760	0.748	0.727	2.20	6.20	10.51	10.65	10.91
I50P25	0.865	0.789	0.765	0.758	0.745	2.35	6.05	7.35	8.75	9.15
I50P35	0.805	0.785	0.783	0.762	0.749	2.55	5.85	8.75	9.55	9.95
I50P50	0.811	0.788	0.760	0.742	0.729	2.85	5.95	8.55	9.55	11.95

**Table 4** Average value  $k_1$  of the concrete mixed with ground palm oil fuel ash at various exposure times in marine site

Ground palm oil fuel ash content (%)	The average value $k_1$				
	1 year	3 years	5 years	7 years	10 years
0	0.778	0.736	0.727	0.712	0.708
15	0.843	0.786	0.766	0.758	0.747
25	0.855	0.793	0.783	0.776	0.764
35	0.837	0.792	0.781	0.763	0.754
50	0.836	0.785	0.758	0.744	0.733



**Fig. 3** Regression analysis between  $k_1$  and exposure time ( $t$ ) in palm oil fuel ash concrete

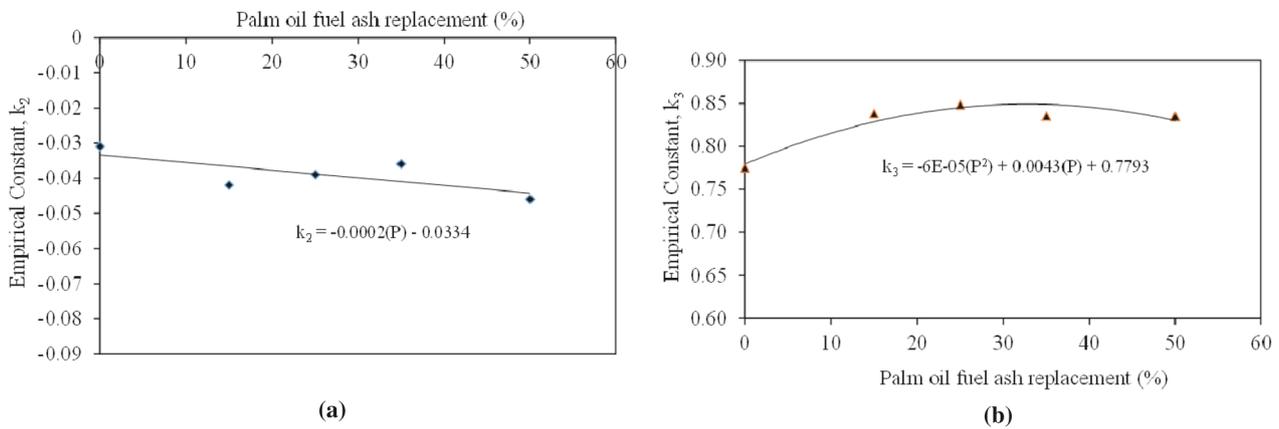
structures with unidirectional chloride penetration. This is because the chloride content data in concrete were collected at the center core of each cubic specimen which has  $200 \times 200 \times 200 \text{ mm}^3$  dimensions. It was also assumed

that chloride penetrated in downward direction from the surface. Appropriate structures under these assumptions are floor slabs, foundations or other concrete structures that are penetrated by chloride ion in one direction.

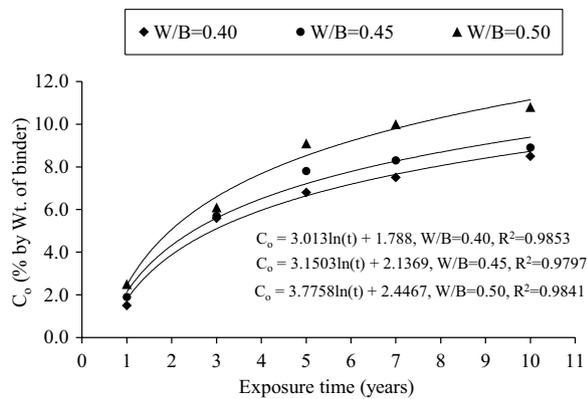
#### 4 Model Verification

Result comparisons of chloride contents between the established model and actual data collected from different exposure times of 5, 7, and 10 years have been made. Chloride contents in concrete at 5, 15, 25, 35, 45, 55, 65, 75, 85, and 95-mm depth were used to compare with the model as shown in Fig. 7. The results show that the margin of errors within  $\pm 35\%$  range, where the percentage error appeared to be higher at the greater depth from the concrete surface. This is because the low chloride content in the concrete results in a sensitive percentage error. However, this comparison is only a part of model development process that shows reasonable prediction results compatible with the available database.

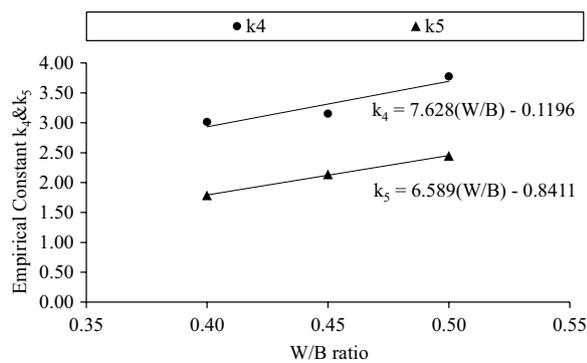
Therefore, result verification should be done by comparing these results with ones reported by other researchers (Kim et al., 2016; Mohammed et al., 2003; Nanukuttan et al., 2015). In this study, chloride penetration due to the marine environment in palm oil fuel ash concrete were lacking from other research studies. Therefore, the predicted chloride penetration in conventional concrete (Portland cement type I concrete) was compared with other studies under a marine environment of up to 30 years under similar conditions as shown in Fig. 8. It was found that most of the predicted chloride content yields higher than the actual test results.



**Fig. 4** Regression analysis between (a)  $k_2$  and (b)  $k_3$  values and ground palm oil fuel ash content. **a**  $k_2$ , **b**  $k_3$



**Fig. 5** Relationship between the average of  $C_0$  and exposure time ( $t$ ) of palm oil fuel ash concrete under marine site



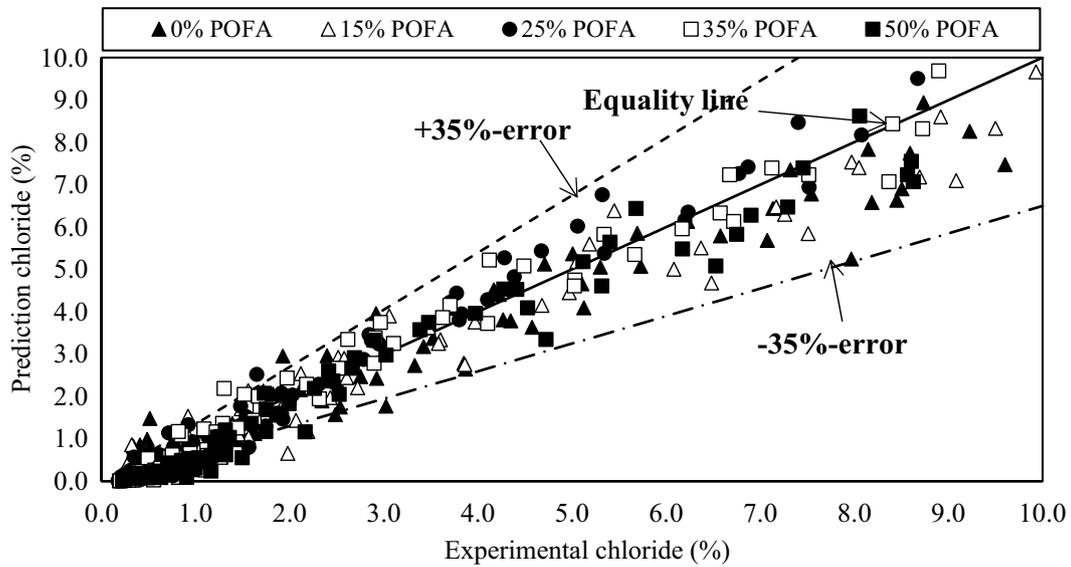
**Fig. 6** Relationship between the  $k_4$  and  $k_5$  coefficients and the W/B ratios of palm oil fuel ash concrete under marine site

### 5 Model Applications

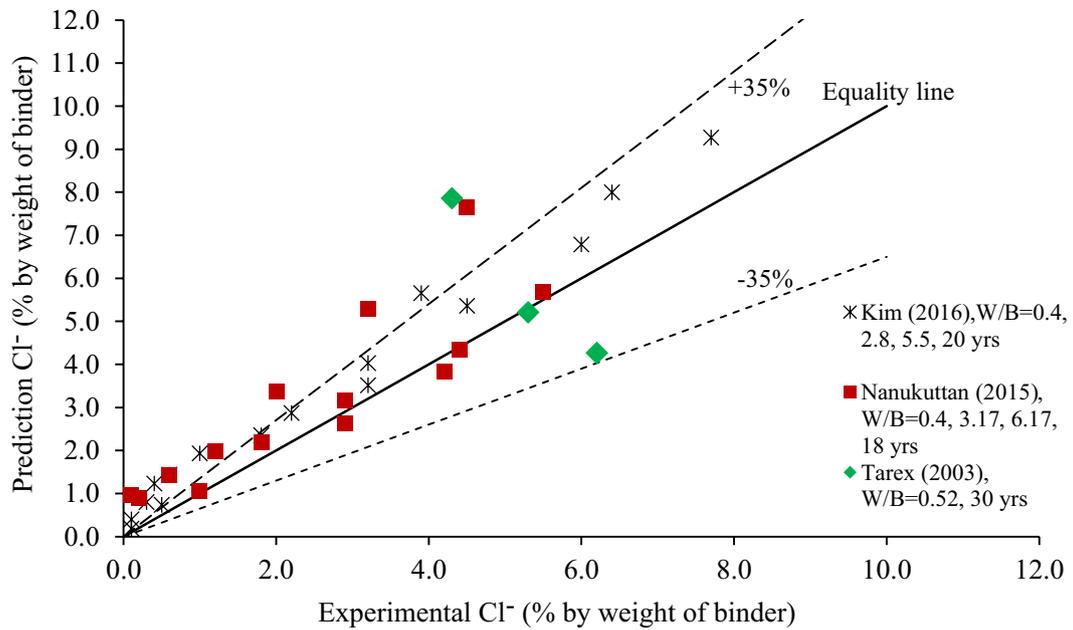
The established model was able to predict total chloride penetration into conventional concrete and concrete containing ground palm oil fuel ash that has been exposed to marine environment. *An example of the proposed model application is shown in Fig. 9.* Fig. 9 shows the predicted chloride penetration in concrete with W/B ratio of 0.40 after 30 years exposure in marine site. The predicted results show that chloride penetration in concrete tend to decrease when using ground palm oil fuel ash in concrete of not more than 35% by weight of binder, while the substitution of up to 50% resulted in a higher chloride penetration. This predicted results consistent trend with the chloride ingress in similar concretes, when immersed in real sea water for up to 7 years (Chalee et al., 2021a, 2021b).

Besides, results obtained from this model can be used for specifying concrete covering depth under the required initial corrosion period *so as to withstand this type of environment in tropical climate zone.* An application of the established model was illustrated for evaluation of the initial corrosion time of reinforced concrete under the marine environment as shown in Fig. 10. Based on the established model, the total chloride content in conventional concrete and concrete containing ground palm oil fuel ash at 10%, 20%, 30%, and 40% by weight of the binder with W/B ratio of 0.40 at the 75 mm depth were presented. The threshold chloride value of 0.51 from the previous research (Yang et al., 2021) was used to estimate the initial corrosion time in concrete under the marine environment. The initial erosion times of conventional concrete and concrete mixed with ground palm oil fuel ash of 10%, 20%, 30% and 40% by weight of binder with W/B ratio of 0.40 and covering depth of 75 mm were 7, 12, 16, 19 and 17 years, respectively.

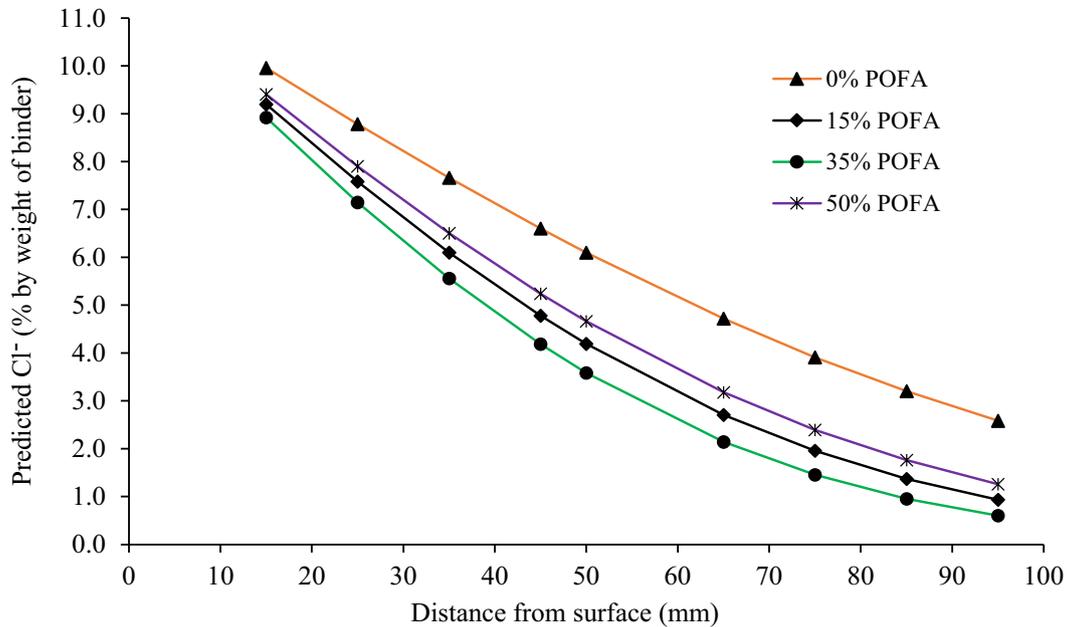
However, most of the predicted results of chloride content from this model compared to the other studies give a margin of errors within  $\pm 35\%$  range.



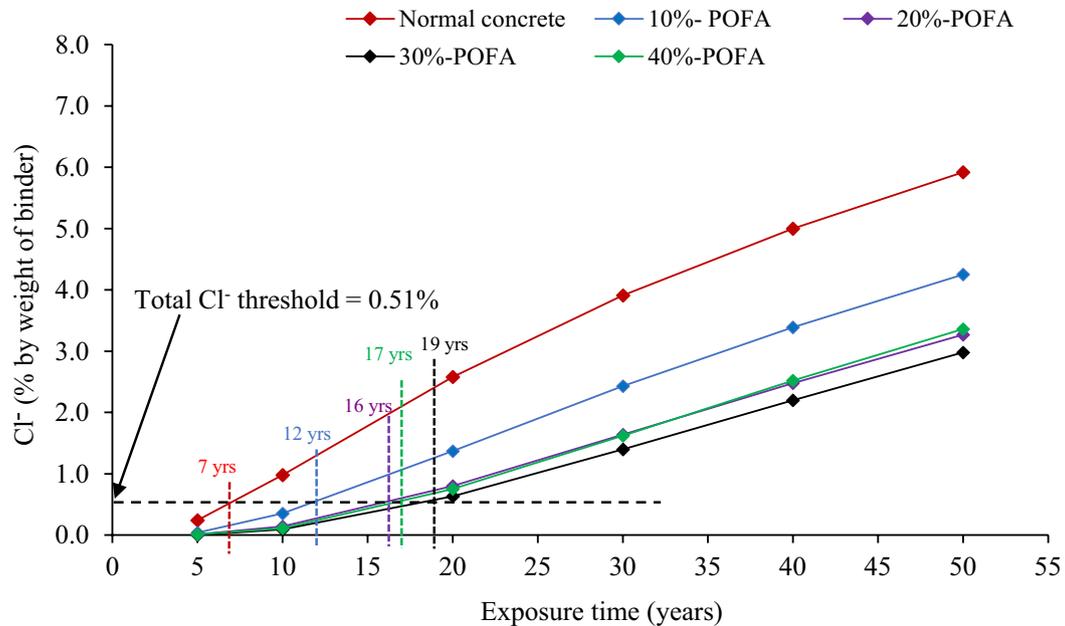
**Fig. 7** Comparisons of chloride contents between the established model and actual data collected at exposure times of 5, 7, and 10 years



**Fig. 8** Comparisons of chloride contents between the established model and actual data of normal concrete collected from another research



**Fig. 9** The predicted total chloride penetration into concrete mixed with ground palm oil fuel ash with a W/B ratio of 0.40 after 30 years exposure in marine site



**Fig. 10** Evaluation initial corrosion time of reinforced concrete with W/B ratio of 0.40 and 75-mm covering depth under the marine environment

**6 Conclusions**

In this study, the empirical model to predict chloride penetrations in concrete containing ground palm oil fuel ash under marine environment was proposed. The developed empirical model can predict total chloride content at any position below the surface of concrete, which has

been submerged under sea water for 1 year and over. The model is applicable for either conventional concrete (Portland cement type I concrete) or concrete containing ground palm oil fuel ash not greater than 50% by weight of binder. The W/B ratio is also limited between 0.40 and

## 0.50 which are the specified W/B ratios for concrete in the marine environment.

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### Author contributions

The authors investigated the test results and studied the mechanism of durability performance as well as generating the prediction model in this study. All authors read and approved the final manuscript.

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Not applicable.

### Availability of data and materials

All data used during the study appear in the submitted article.

### Declarations

### Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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