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Mathematical Optimization of the Anti-Corrosive Rice Husk Ash Enhanced Concrete under Marine Environment

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Chloride induced steel corrosion causes safety and stability problems to the reinforced concrete structure located closed to or under marine environment. The corrosive steel rust could potentially lead to surface swelling altering the external appearance, generating the concrete cracking, lowering the elasticity, reducing tensile strength, and thus leading to the deterioration of the concrete structure. Recent studies present an innovative method for inhibiting chloride corrosion by the addition of fibres into concrete to improve its toughness and tensile properties. By the addition of high fineness rice husk ash (RHA), the RHA would function as chloride adsorbent, preventing the chloride penetration through the concrete into the steel foundation. However, the addition of the RHA also affects the compressive strength, the workability, the consistency, and the slump of the concrete structure, limiting the mixed amount of the RHA that could be added in the concrete. A linear optimization model of the anti-corrosive RHA enhanced concrete has been formulated with the objective to minimize the effect of the chloride corrosion of the steel; whereas, the amount of the mixed RHA is limited by the critical concrete strength in term of modulus elasticity. In this study, the mass transfer coefficient, adsorption coefficient, and the Langmuir equilibrium isotherm are taken from the literatures. The chloride concentration is assumed to be 3.5 % w/v of the total chloride ion in salt water. The model has been validated with the measured data collected from open literatures. The optimum ratio between the RHA and cement mixture is discovered to be based on the void fraction of the concrete mixture. The optimum ratio is found to be around 10 % at the void fraction 0.8 and increasing to 25 % at the void fraction 1.2.

1. Introduction

Concrete is a composite material widely used in construction due to its high compressive strength, durability and low price. However, the disadvantage of concrete is its low resistivity to tensile force (low tensile strength). Thus, the reinforced concrete has been invented for increasing the tensile strength of the material by embedding the steel inside the plain concrete (Park and Paulay, 1975).

Due to the dissolved ions in the seawater, the concrete structures installed in or closed to the marine environment are severely deteriorated, affecting the strength, structural lifetime and the appearance of the structure (Alonso et al., 1998). Nowadays, the Portland cement type 5 containing tricalciumaluminate

 $(3CaO \cdot Al_2O_3: C_3A)$ is used for the construction in the seawater because it can resist sulfate salts (SO_4^{2-}) (Otieno

et al., 2011). Indeed, seawater is composed of 10 % sulfates and 90 % chlorides (Cl⁻). In which, chloride is the main factor leading to corrosion of the steel in the reinforced concrete (Ahmad, 2003). The chloride-induced steel corrosion causes the structures to lose their durability in term of mechanical force endurance, fatigue and bending resistances. Finally, the plain concrete is cracked and is not able to resist the mechanical force anymore (Berrocal et al., 2016). Therefore, many solutions have been developed for decelerating and solving this problem; one of an interesting method is the addition of pozzolanic material as a binder in order to resist chloride diffusion in plain concrete (Horsakulthai et al., 2011).

The pozzolanic materials mainly comprise silica (SiO₂), alumina (Al₂O₃) and iron oxide (Fe₂O₃). Generally, dry pozzolanic materials are dust-like without cementitious property between the particles. On the contrary, with enough humidity, the pozzolanic materials in normal atmosphere would react with calcium hydroxide (Ca(OH)₂)

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and form a new compound which has a good cementitious property. These reactions (1) and (2) are called pozzolanic reactions (H. Dodson, 1990).

$$Ca(OH)_2 + SiO_2 + H_2O \rightarrow xCaO \cdot ySiO_2 \cdot zH_2O$$
(1)

$$Ca(OH)_2 + Al_2O_3 + H_2O \rightarrow xCaO \cdot yAl_2O_3 \cdot zH_2O$$
(2)

The pozzolanic materials are able not only to partly replace the cement in the concrete but also to improve the properties of concrete such as compressive strength and durability in various environments (Shatat, 2016). Also, the production cost of concrete is reduced because the pozzolanic materials are cheaper than the cement (Zareei et al., 2017).

As an agricultural country, there are many agricultural wastes produced daily in Thailand; especially rice husk ash (RHA). According to the research of Chatveera and Wongkamjan (2001), the main composition of RHA is silica, which could be used as the pozzolanic component in the cement mixture; especially amorphous RHA which has the better pozzolanic reactivity than that of crystalline RHA. However, too high percentage of the RHA replacement in concrete reduces the mechanical properties of the materials even the corrosion resistivity increases (Chatveera and Wongkamjan, 2001). Therefore, in this work, the mathematical model was developed to find the optimum replacement percentage of RHA that provides a good compressive strength of reinforced concrete while salt corrosion due to chloride ions are decelerated as much as possible.

2. Model development

The modelling methodology developed by Cameron and Gani (2011) has been applied for the development of the optimization model for the RHA enhanced concrete. The developed model is divided into 3 parts: balance equations, constitutive equation, and conditional equation.

2.1 Balance equations

The physical system in consideration is illustrated in Figure 1. The mass conservation law is applied to the incremental volume of the concrete with the length dz. To calculate the concentration profile and the penetrated chloride concentration within the concrete body, following assumptions are adopted:

- a. The concentration of the chloride in the bulk of sea water is lumped from different chloride-binding chemical species as average chloride ion concentration and treated equivalently.
- b. The RHA is uniformly distributed throughout the concrete body.
- c. The average porosity is assumed at all location within the concrete body.
- d. The effect of the pressure drop within the concrete body is neglected.
- e. The variation of chloride concentration is in z-direction only and is uniform at x-y plane of the bed.
- f. The absorptive heat transfer is neglected.
- g. The effect of the penetrated moisture is lumped together with the penetrated chloride ion
- h. The dispersions of the chloride concentration in x-y directions are neglected.



Figure 1: Physical illustration of the RHA enhanced concrete adsorption system

Applying the balance equation on the chloride concentration, the equation for the penetrated chloride is displayed in Eq(3) and the accumulation of the chloride in the solid-phase RHA is displayed in Eq(4).

$$\frac{\partial C_{Cl}}{\partial t} = D_{Cl} \frac{\partial C_{Cl}}{\partial z} - hA(C_{Cl} - C^*)$$
(3)

$$\frac{\partial Q_{Cl}}{\partial t} = V_m \frac{\dot{n}_{Cl}}{m_s} \frac{\partial C_{Cl}}{\partial z}$$
(4)

where D_{Cl} is the mass transfer coefficient of the chloride in the concrete, *h* is the adsorption coefficient of the chloride in the RHA, *A* is the surface area of the RHA, Q_{cl} is the active molar concentration of the chloride adsorbed in the RHA, V_m is the molar volume of the chloride in the RHA, m_s is the RHA mass, \dot{n}_{cl} is the chloride adsorption flux, and C_{cl} and C^* are the concentration of the chloride ion in the concrete and the equilibrium equivalent concentration of the chloride in the RHA.

2.2 Constitutive equation

The constitutive equation of the absorption is derived from the Langmuir adsorption isotherm (Sandberg et al., 2017) as presented in Eq(5).

$$C^{*} = \frac{0.472 P_{Cl^{-}}^{Sat}(T_{SW})}{P_{SW} - 0.612 P_{Cl^{-}}^{Sat}(T_{SW})}$$
(5)

where T_{sw} is the salt water temperature, P_{sw} and P_{CT}^{Sat} are the salt water saturated pressure and chloride ion saturated pressure.

2.3 Conditional equation

The amount of the mixed RHA is limited by the associated conditional equation maintaining the concrete modulus elasticity above the critical limit (Sukjinda, 2016) which are directly related to the ratio between the RHA and the cement mixture (γ) as displayed in Eq(6).

$$K = \frac{\lambda(1+\nu)}{3\nu} \propto \gamma \tag{6}$$

where K is the bulk modulus, λ is the Lamé parameters, v is the Poisson's ratio.

2.4 Optimization equations

The model is formulated as linear optimization model minimizing the effect of the chloride corrosion of the steel as displayed by the following Eqs(7) to (11).

$\min z = f(x)$	(7)
g(x) = 0	(8)
$x \in X$	(9)
$h(x) \ge 0$	(10)

$$x^{LO} \le x \le x^{UP} \tag{11}$$

where *z* represents the penetrated chloride concentration at the steel bar, which is subjected to subject to equality (*g*) and inequality (*h*) constraints such as the calculation of equilibrium equivalent concentration of the chloride in the RHA and the minimum concrete modulus elasticity, the variable *x* is defined as a variable in the continuous region (*X*) that have upper (x^{UP}) and lower (x^{LO}) bounds representing the design and operating variables, such as the amount of the RHA and the concentration of the penetrated chloride.

3. Numerical procedure

ICAS-MoT (Integrated Computer Aided System – Modelling Testbed) (Sales-Cruz and Gani, 2003) has been used for the construction, analysis, and solving the model.

- The optimizations and parameters regressions are solved using the successive quadratic programming (SQP) based method incorporated in the software.
- The 5th order backward differential formula (BDF), the implicit Runge-Kutta method, and the forward multistep Euler method have been applied for solving the ordinary differential equations based on the stability of the results obtained.

4. Results

4.1 Model validations

The compressive strength has been calculated by the Eq(6) at various void fractions and percentage of mixed-RHA. The model calculations have been validated by the measured data taken from literatures. The measured RHA-enhanced concrete compressive strengths after 28 days with the percentage of RHA between 0 to 20 are reported by Sangsuwan (2013). Jaturapitakkul (2011) also reported the concrete compressive strengths after 28 days and 5 years with 2 different void fractions (0.8 and 1.2), and percentage of RHA between 0 to 45. Similarly, Chatveera and Wongkamjan (2001) measured the compressive strengths of concrete with void fractions between 1 to 1.6 and percentage of RHA between 0 to 40. The comparison between the measured and calculated compressive strength after 28 days is displayed in Figure 2, the average absolute deviation is less than 1.3 % with maximum deviation less than 3.1 %.



Figure 2: Comparison between calculated and measured compressive strength



Figure 3: Comparison between measured and calculated penetrated chloride concentration at the steel surface at various RHA mixed percentage

Meanwhile, the penetrated chloride concentrations at the steel surface at different submerged period with different blended RHA percentages are calculated by Eqs(3) to (5). The calculations have been validated also by the data from open literatures. The penetrated chloride concentrations at the steel surface after 28 days are report by Sangsuwan (2013); Chalee et al. (2013) report the concrete chloride concentration after 28 days and 5 years submerged under marine condition; and Medeiros et al. (2013) report the chloride content and corrosion rate of the concrete column at different level. Figure 3 displays the comparison between measured and calculated penetrated chloride concentration at the steel surface; in total, the average absolute deviation is less than 2.5 %. The shapes of the concentration developments are following typical adsorption behavior. These results confirm that the model is valid and applicable for predicting the chloride penetration and the concrete properties of this system.

4.2 Optimization of the mixed RHA percentage

The validated model has been applied for calculating the optimum mixed-RHA percentage under the constraint that the compressive strength of the enhanced concrete should be higher than 80 % that of the plain concrete mixture. As displayed in Figure 4, the concrete strengths varying depending on the void fractions, the RHA at low concentration help binding the concrete mixture thus heightening the compressive strength; however, increasing the percentage of RHA in the mixture leads to sharp decrease of the concrete strength. The greyed-out area in Figure 4 present the minimum compressive strength limit, in the concrete mixture with void fractions of 0.8 and 1, percentage of the mixed RHA should not exceed 10 %; while the mixture with void fraction of 1.2 and above, the percentage of the mixed RHA could be as high as 25 % or more.



Figure 3: Calculated compressive strength at different mixed-RHA percentage and void fractions

The chloride breakthrough curves for the concrete and RHA-enhanced concrete with different void fractions are presented in Figure 5; as expected, the breakthrough time for the concrete with lower void fraction is higher. The mixed-RHA has higher effect toward the concrete with larger void volume. The effect of the mixed-RHA begin deteriorating fast with the low-void concrete.



Figure 4: Chloride breakthrough time at different concrete void fractions and mixed-RHA percentages

Considering Figures 4 and 5 together, it can be concluded that the optimum amount of the mixed-RHA varying with the concrete mixtures characteristic. With void fraction below 1.0, less than 10 % of RHA should be blended into the concrete body. On the contrarily, with the concrete void fraction above 1.4, the optimum percentage of RHA is well above 25 %; however, considering other aspect of the concrete such as the appearance, the settling time, and the shear modulus, the percentage of mixed-RHA should not exceed literature measured value, until more data available.

5. Conclusions

The model for predicting the compressive strength and the adsorptive capacity of the RHA-enhanced concrete has been developed and validated with available measured data. The model is shown to be in a good agreement with the collected data. To demonstrate the applicability of the model, it has been initially adopted for estimating the optimum percentage of the RHA to blend into the concrete mixture to achieve the maximum chloride protection as well as maintain the concrete strength. However, other aspect of the concrete properties should also be considered before fully adopted this model for the prediction of the optimum percentage of the mixed-RHA. Nonetheless, the experiment is being conducted to confirm the preciseness of the model; as well as, to include other concrete properties into the database for further consideration.

References

- Ahmad S., 2003, Reinforcement corrosion in concrete structures, its monitoring and service life prediction—a review, Cement and Concrete Composites, 25, 459–471.
- Alonso C., Andrade C., Rodriguez J., Diez J.M., 1998, Factors controlling cracking of concrete affected by reinforcement corrosion, Materials and Structures, 31, 435–441.
- Berrocal C.G., Lundgren K., Löfgren I., 2016, Corrosion of steel bars embedded in fibre reinforced concrete under chloride attack: State of the art, Cement and Concrete Research, 80, 69–85.
- Cameron I.T., Gani R., 2011. Product and process modelling: a case study approach, Elsevier Science, Amsterdam, Netherlands.
- Chalee W., Sasakul T., Suwanmaneechot P., Jaturapitakkul C., 2013, Utilization of rice husk-bark ash to improve the corrosion resistance of concrete under 5-year exposure in a marine environment, Cement and Concrete Composites, 37, 47–53.
- Chatveera B., Wongkamjan W., 2001, Mechanical behavior of fine RHA concrete, KMUTT Research and Development Journal, 24, 327-342.
- H. Dodson V., 1990, Concrete admixtures, Springer, Boston, USA.
- Horsakulthai V., Phiuvanna S., Kaenbud W., 2011, Investigation on the corrosion resistance of bagasse-rice husk-wood ash blended cement concrete by impressed voltage, Construction and Building Materials, 25, 54–60.
- Jaturapitakkul C., Chalee W., 2011, Chloride binding capacity of concrete containing rice husk bark ash under marine environment, KMUTT Research and Development Journal, 34, 245-255.
- Medeiros M.H.F., Gobbi A., Réus G.C., Helene P., 2013, Reinforced concrete in marine environment: Effect of wetting and drying cycles, height and positioning in relation to the sea shore, Construction and Building Materials, 44, 452–457.
- Otieno M.B., Beushausen H.D., Alexander M.G., 2011, Modelling corrosion propagation in reinforced concrete structures A critical review, Cement and Concrete Composites, 33, 240–245.
- Park R., Paulay T., 1975, Reinforced concrete structures, John Wiley & Sons Ltd., Christchurch.
- Sales-Cruz M., Gani R., 2003, A modelling tool for different stages of the process life, Computer Aided Chemical Engineering, 16, 209–249.
- Sandberg T., Weinberger C., Şen Karaman D., Rosenholm J.M., 2017, Modeling of a Hybrid Langmuir Adsorption Isotherm for Describing Interactions Between Drug Molecules and Silica Surfaces, Journal of Pharmaceutical Sciences, 107, 1392-1397.
- Sangsuwan C., 2013, Resistance to chloride permeability of pozzolanic concrete, Research Summary, Rajamangala University of Technology Phra Nakhon, Bangkok, Thailand.
- Shatat M.R., 2016, Hydration behavior and mechanical properties of blended cement containing various amounts of rice husk ash in presence of metakaolin, Arabian Journal of Chemistry, 9, S1869–S1874.
- Sukjinda P., 2016, Optimum black rice husk ash for structural concrete work, Building Innovation 2016, National Institute of Building Sciences, 47-52.
- Zareei S.A., Ameri F., Dorostkar F., Ahmadi M., 2017, Rice husk ash as a partial replacement of cement in high strength concrete containing micro silica: Evaluating durability and mechanical properties, Case Studies in Construction Materials, 7, 73–81.