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MODELLING CARBONATION OF FLY ASH CONCRETE USING SYSTEM DYNAMICS

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Abstract: Steel reinforcement corrosion is the most frequent threat to concrete durability. Carbonation is considered to be one of the prominent precursors to steel corrosion in concrete. The introduction of fly ash concrete increases the amount of hydration product; hence the permeability is less and the durability is improved. In this study, system dynamic software (Vensim PLE) is used to model the carbonation of fly ash concrete. The relations between porosity, diffusivity of carbon dioxide and the carbonation depth are modelled as feedback loops and the influences of significant external factors are also incorporated. The model predicts the carbonation depth propagation over 100 years and the results are validated against the available experimental studies. The model also concludes that the fly ash replacement between 20% and 30% would optimize durability. Carbonation itself creates a balancing loop causing a reduction in the rate of carbonation over the years.

Keywords: Carbonation; Concrete Durability; Fly Ash; Vensim software; Balancing Loop

1. Introduction

Reinforced concrete is the most commonly used building material in building and bridges. Despite the fact that reinforced concrete shows good medium term performance, it deteriorates due to reinforcement corrosion.

Carbonation on the one hand and chloride ingress on the other are the main causes of steel corrosion. Carbonation occurs in concrete because the calcium bearing phases (produced during cement hydration)are attacked by carbon dioxide in the air and converted to calcium carbonate. The reaction is given in Equation (1).

$$Ca(OH)_2 + H_2O + CO_2 \rightarrow CaCO_3 + 2H_2O \qquad (1)$$

Due to the reaction, the alkalinity of the pore solution (pH) reduces. At pH over 12.5, corrosion attacks are usually prevented by a passive coating formed on the steel. As long as the passive coating is sustained, carbonation will not occur. Disruption of the layer due to loss of alkalinity will be initiated by carbonation, which removes OH^- ions from the pore solution. Subsequent accumulation of corrosion products causes concrete cover spalling and other structural deterioration.

Introduction of blended cement for the manufacture of concrete is considered as a sustainability breakthrough in the industry. Blended cements are obtained by mixing Ordinary Portland Cement (OPC) with mineral additives such as fly ash or silica fume. Blended cements have active pozzolanic components that react with the calcium hydroxide to form additional hydration products and directly results in improved durability. Environmental advantages such as energy saving, conservation of natural resources and pollution control can also be achieved by using blended cements rather than pure OPC.

Fly ash is the most common pozzolan in use [1]. Fly ash is the combustion residue from the coal-electric power plants. Two commonly found categories of fly ash are low carbon fly ash and high carbon fly ash. It is generally realized that the use of fine fly ash improves the properties of mortar and concrete [2].

Available durability models do not comprehensively account for all the inter-related factors which affect the fly ash concrete durability. In the present study, a system dynamic model is introduced to understand the positive and negative enforcers of carbonation through causal loop diagrams. Model was developed by incorporating the existing knowledge embedded in mathematical relationships; and validated against the experimental results. The prediction of carbonation depth is presented for 100 years life span.

2. System Dynamics

System dynamics can be defined as a methodology and mathematical modelling technique for framing, understanding and discussing complex issues and problems [3].It was initially developed to aid corporates but has today found application in a wide range of areas. This approach is used in the model to envision the complexity of the interrelationship between the factors influencing the corrosion.

System dynamic approach is a framework where the past behaviour is allowed to influence the system through a feedback loop. These causal closed loops can either be reinforcing or balancing loops depending on whether the rate of the process is accelerated or decelerated. Various software such as Vensim, ASCEND, Pyndamics and Optisim are freely available for educational purposes.

Vensim (PLE) is chosen for this study, as it has been widely accepted. The graphic model construction interfaces of Vensim simplify the representation of mathematical relationships and ease the analytical work. It also incorporates Monte-Carlo estimation and allows the user to vary multiple influencing factors in a given time and plot the sensitivity of the process. [4]

System dynamic has four basic building blocks: stock, flow, connector and converter. These building blocks are used in Vensim software and the applications of the blocks are given inTable1.

3. Carbonation Model Development

The closed loop model has three major components interconnecting each other: depth of carbonation, diffusivity of CO_2 and porosity. The influence of the contributing factors on the major components and inserted into the loop through theoretical expressions.

Table 1: Basic Building Blocks in Vensim [5]

Variable	Functions
Box / Level Variable	Represents Quantities. These are the main nouns in the system.
Rate Variable	Represents a change in quantity over the time. These are the verbs in the system.
Auxiliary Variable	Represents the constants or other parameters. Corresponds to adjectives and adverbs in the system.
Connectors	Illustrates dependencies between variables

3.1 Depth of Carbonation

From Fick's law, Neville [6] introduced carbonation depth as the quantitative measurement of the carbonation severity and proposed that the depth is proportional to the square root of time as given in Equation (2).

$$x = \sqrt{\frac{2Dc}{a}}\sqrt{t} \tag{2}$$

Here$x$ is the carbonated depth at time t, D the effective diffusivity of CO2, c is the concentration in the atmosphere and a the concentration of the supplementary cementitious materials (SCM) such as fly ash.

Various approaches were further tried to improve the accuracy of the equation by considering water cement ratio, temperature and moisture content [7]. Papakadis and Tsimas [8] proposed an empirical equation as shown in Equation 3.

$$x_c = \sqrt{\frac{1.09 D_{e,Co2} C_{co2} 10^{-6} t}{0.218\,(c + kP)}} \tag{3}$$

Here C_{co2} is the CO_2 content (mgm^{-3}), k is the efficiency factor of the SCM and $D_{e,Co2}$is the effective diffusivity of CO_2 in carbonated concrete ($m^2\ s^{-1}$). P and care the SCM and cement content in the initial concrete mix ($kg\ m^{-3}$) respectively.

The influence of relative humidity (RH) on carbonation is proposed by Venuat [9]. He observed that the maximum penetrations appear when RH is between 50% and 65% and developed a function for RH against the depth of carbonation. The function is interpreted by Teply et al [10] as in Equation (4) and incorporated into Equation (3) and the resulting Equation (5) is arrived.

$$f(RH) = -9.1766RH^4 + 18.941RH^3 - 15.539RH^2 + 6.1876RH - 0.0094 \quad (4)$$

When RH increases, the saturation ratio of the pore solution increases and carbon dioxide diffusion is hindered; hence the carbonation reaction is slowed down. However, existence of water is a necessity for the reaction to occur. This explains why the polynomial curve defined mathematically passes through a maximum.

$$x_c = \sqrt{\frac{1.09 \times D_{e,Co2} C_{co2} 10^{-6} t}{0.218\,(c + kP)} f(RH)} \quad (5)$$

Under the atmospheric conditions, CO_2 content is considered to be 680mgm^{-3}. Equation (5) is adopted into the model and a direct relationship with the diffusivity of CO_2 is maintained. Time function is also incorporated into the model through this equation.

3.2 Diffusivity of CO_2

The intrinsic diffusion rate at which ions or molecules are transported in concrete depends on the size and connectivity of the pore system. Papadakis[11] introduced the empirical relationship fitted to the experimental values between the porosity (ε) of the concrete and the effective diffusivity of carbon dioxide as given in Equation (6).

$$D_{e,Co2} = 1.64 \times 10^{-6} \varepsilon^{1.8} \times 0.218 \quad (6)$$

He primarily developed these values for OPC concrete of water cement ratio between 0.3 and 0.8 but later tested for various fly ash concretes and concluded that the equation applies equally well. The secondary effects of RH are considered to be independent of binder type.

3.3 Concrete Porosity

It is generally realized that the porosity of the concrete is directly attributable to the water cement ratio. The fly ash replacement will also affect the porosity although the reduction in porosity due to pozzolanic activity is smaller than that due to hydration of the same quantity of OPC [11]. This effect will initially increase in the porosity but in the long run, fly ash concrete porosity will be reduced through the pozzolanic reactions.

Lam et al [12] developed a linear relationship between gel/space ratio and porosity of concrete by curve fitting as given in Figure 1. Gel/space ratio is defined by the degree of hydration of cement and the efficiency of SCM material. The gel/paste ratio is defined by the Equation (7).

$$x_{fc} = \frac{2.06 v_c \alpha_c c + 2.5 v_f \alpha_f f}{v_c \alpha_c c + v_f \alpha_f f + w} \quad (7)$$

The c, w and f stand for cement, water and fly ash content respectively. Specific volume of cement and fly ash is denoted by v_c and v_f. Similarly, the degree of hydration and the efficiency of fly ash is denoted by $\alpha_c$and α_f.

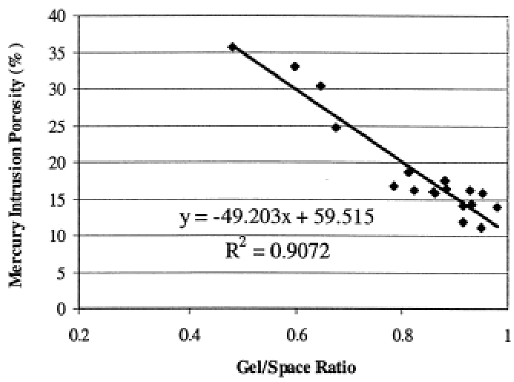

Figure 1: Porosity vs Gel/Space ratio [12]

Therefore, degree of hydration and the efficiency of the fly ash is further analysed to simplify the model application.

Lam [12] et al also used experimental data to calculate the degree of hydration and proposed it as a function of water binder ratio in Equation (8).

$$\alpha_c = a \times e^{\frac{b}{w-b\,ratio}} \quad (8)$$

He measured the parameters after 7, 28 and 90 days quantified the unknown constants a and b. By exploring his results using curve fitting technique, Equation (9) was obtained.

$$\alpha_c = 1.0737 \times e^{\frac{-1.0405}{w-b\,ratio}} \qquad (9)$$

The efficiency of fly ash will depend on the age and the replacement percentage [13]. Babu and Rao [14] proposed a total efficiency factor α_f for the long term low calcium fly ash replacement model as in Equation (10).

$$\alpha_f = 2.54p^2 - 3.62p + 1.73 \qquad (10)$$

Here p represents the percentage low calcium fly ash replacement of the cement.

$CaCO_3$ is the product of carbonation process and it will fill up the available pore space and reduce the porosity further [15]. This porosity reduction due to the carbonation process in turn reduces the diffusivity of CO_2 and transforms the carbonation system into balancing loop. It is this kind of incremental reduction in rate constants (in this case CO_2 diffusivity) that make Vensim type approaches very appropriate.

In order to account the effect of porosity reduction, experimental results given by Dias [16] are used (assuming linearity) as a multiplying factor (F_ε) on initial porosity as in Equation (11).

$$F_\varepsilon = \frac{9.84 - (0.08 \times x_c)}{9.84} \qquad (11)$$

Hence porosity can be written as follows.

$$\epsilon = (-49.203 \times \text{gel/space ratio} + 59.515) \times F_\varepsilon \qquad (12)$$

3.4 Carbonation Vensim Model

All the above equations were incorporated into the Vensim model with appropriate units and the in-built internal checks applied by the software. The model is shown in Figure 2. Predictions were made for carbonation depths over a lifespan of 100 years.

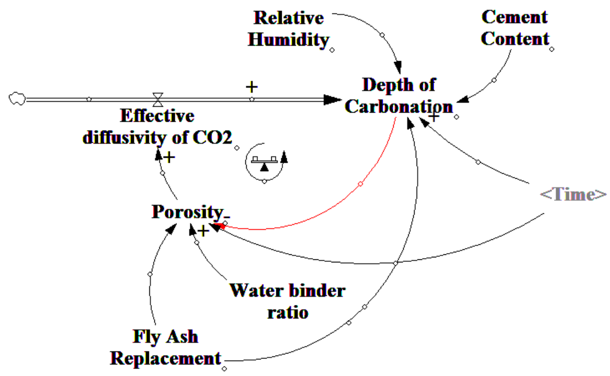

Figure 2: Vensim Carbonation Model

The model is developed to predict two cases where (i) the porosity of the concrete is reduced by the carbonation itself [16], as described above (Model A); and (ii) where the effects proposed in [16] are not adopted (Model B). For this latter case, Equation (12) can be rewritten as Equation (13) shown below.

$$\epsilon = (-49.203 \times \text{gel/space ratio} + 59.515) \qquad (13)$$

4. Validation of the Model

The results were validated against a study carried out in Portugal by Costa and Appleton [17]. This study is completely independent from the equations used to build the model.

Two mix compositions (C1, C2) were used in this experiment to develop time functions for carbonationfrom the results of carbonation depths recorded over the first 6 years.

Mix compositions did not include fly ash. Cement content of 300 kgm^{-3} and water binder ratio of 0.5 were used for the C1 mix, whereas C2 mix had the corresponding parameters of 425 kgm^{-3} and 0.3 respectively.

The results obtained had been modelled in two ways. The first model assumed the carbonation depth as proportional to the square root of time [6]. In the second model, a best fit curve is arrived at with the exponent of time allowed to vary. This exponent was found to be 0.44 for mix C1 and 0.40 for mix C2 (see Table 2). The reduction in the n value below the 0.5 derived from Fick's law can be attributed to the incremental reduction in the CO_2 diffusivity.

These are compared with those obtained from the Vensim model. Model C1-A represents the C1 mix used in [17] where porosity reduction due to carbonation is accounted for; whileModel C1-Bdoes not. Models C2-A and C2-B are also similarly defined for the C2 mix. In computing percentage differences for the 100 year (predicted) values, the Model B outputs are compared with Costa and Appeton results [17] that assume Fick's law (time exponent is 0.5) and the Model A outputs with those that allow the time exponent to fall below 0.5.

Figure 3 gives graphical representations, where the Model B results are consistently lower than the Model A ones.

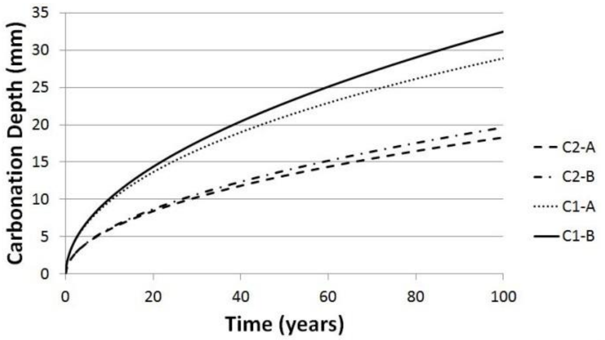

Figure 3: Carbonation depth vs Time (Vensim)

5. Discussion

System dynamic thinking implements reinforcing and balancing loops where the effects of past behaviour increase and decrease the rate of action respectively. In the carbonation model, continuous reactions will produce more $Ca(CO)_3$ that will fill the pore spaces, causing the carbonation rate to reduce with time. Therefore, this phenomenon is considered a balancing loop in system dynamics

The effect of change in porosity reduction with time is carried out in the study and the results are presented in Figure 3 and Table 2. The carbonation depth is higher when the porosity reduction is neglected. The model outputs display reasonable agreement with the experimental results (and their extrapolations).Model B outputs appear to show slightly better fit with results. However, we argue that Model A is theoretically superior, because it has a mechanism for the exponent of time to be under 0.5[17].

Sensitivity analyses were carried out for each control variable present in the model and the behaviour patterns of both model conditions were identified. Table 3 presents the changes in carbonation depth with water binder ratio when cement content is 300 kg/m^3 and RH is 80%.

Table 2: Validation of the Vensim carbonation model

Type	Duration	Costa & Appleton (2001)		With porosity reduction (Model A)		Without porosity reduction (Model B)	
C1	6 years	Experimental	9mm	7.53 mm	16.3%	7.73 mm	14.1%
	100 years	$x = k_1 * t^{0.5}$	36mm	28.9 mm	12.4%	32.5 mm	9.8%
		$x = k_2 * t^{0.44}$	33mm				
C2	6 years	Experimental	5mm	4.60 mm	8.0%	4.67 mm	6.6%
	100 years	$x = k_1 * t^{0.5}$	20mm	18.2 mm	13.8%	19.5 mm	2.3%
		$x = k_2 * t^{0.40}$	16mm				

Table 3: Water binder ratio effects on models

w/b ratio	Model A (mm)	Model B (mm)	% difference
0.3	20.7	22.5	7.8%
0.4	24.7	27.2	9.4%
0.5	27.9	31.24	10.6%
0.6	30.6	34.6	11.7%
0.7	32.7	37.4	12.6%
0.8	34.5	39.8	13.3%

The differences between the values from the two models increase as the carbonation depth increases. When the water binder ratio is higher, the large pores allow more CO_2 molecules to react with OH^- ions. More $CaCO_3$is produced and accumulated hence the porosity reduction is significant.

It is also instructive to compare these results with the field observations reported by Dias [18]. When the square root of time law is used for structures ranging from 7 to 125 years of age (all of OPC only concrete), the 100 year carbonation depth from the fitted line suggests a carbonation depth of 49 mm, which is admittedly a little more than predicted by even the 0.8 w/c ratio; this may be because of workmanship deficiencies. However, for structures from 7 to 30 years of age (i.e. more recent concretes), the predicted 100 year carbonation depth is 34.5 mm, very close to the values in Table 3 between w/c ratios of 0.6 and 0.8; note once again that the model outputs would be expected to under-predict field carbonation depths, because the latter would suffer from workmanship defects.

The addition of fly ash into the cement manufacturing can also be studied. Model A is used to plot the variations. Rest of the factors (water binder ratio, cement content, RH) are kept constant (0.5, 425 kgm^{-3}, 0.6 respectively) and carbonation variation against the fly ash replacement is plotted. The results are provided in Table 4. Fly ash replacement against carbonation depth graph is plotted in Figure 5.

From Figure 4, it can be observed that an optimum fly ash percentage can be arrived at with respect to carbonation resistance. The model predicts low carbonation depths when fly ash replacement is maintained between 20% - 30%.

Table 4: Fly ash effects on Carbonation Model

Fly ash (%)	Carbonation Depth (mm)
0	24.7
10	19.8
20	17.8
25	17.5
30	17.6
40	18.6
50	20.1

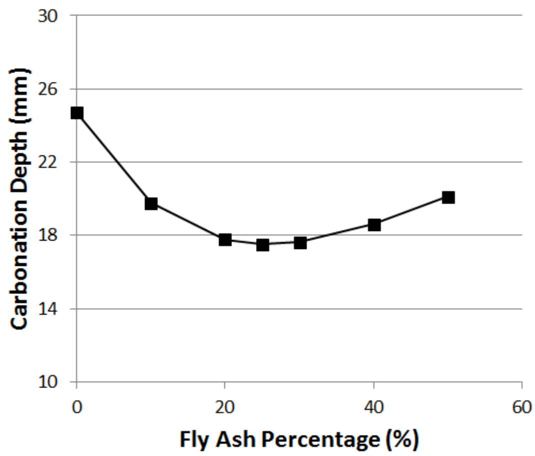

Figure 4: Depth of Carbonation vs. Fly Ash Percentage

6. Conclusion

The following conclusions can be made from this research.

- The carbonation rate decreases with time due to the accumulation of $Ca(CO)_3$ in the pores and the consequent reduction of CO_2 diffusivity. This rate change is identified as a balancing loop in system dynamics; and is associated with a reduction in the exponent of the time function to below the 0.5 suggested by Fick's Law
- The model outputs show good agreement with the experimental results and also field data, although the latter would be under-predicted by the models that do not incorporate workmanship deficiencies.

- For mixes susceptible to carbonation (e.g. higher water binder ratios), the differences between the values from Models A and B are more significant.
- By using low calcium fly ash replacement between 20% - 30% of the cement, the carbonation depth can be reduced by around 30%.

Future studies will extend the system dynamics application to effects such as chloride ingress and its effect on crack width. This would be an example of a reinforcing loop.

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