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Modelling of Chemical Durability Parameter of Fly ash Blended Concrete

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Abstract— In this work the durability of Portland cement systems incorporating fly ash is investigated. The chemical durability issues including carbonation, chloride attack and sulphate attack were studied in detail. This work mainly aims at developing the models connecting the relative durability parameter and the oxide compositions of binder such as silicon di oxide, iron oxide, alumina and calcium oxide and the control ratios of the binder using the data collected. The models were developed using the multiple linear regression analysis. Also the validations of the model are included in the study.

Index Terms— Carbonation, Control ratios, Corrossion, Diffusion, Durability, Fly ash, Sulphate attack

1 INTRODUCTION

Concrete is the most widely used man-made building material in the world, owing to its versatility and relatively low cost. Concrete has also become the material of choice for the construction of structures exposed to extreme conditions. Furthermore, sustainability has become an increasingly important characteristic for concrete infrastructure, as the production of Portland cement is an energy-intensive process that accounts for a significant portion of global carbon dioxide emissions and other greenhouse gases. As such, even slight improvements in the design, production, construction, maintenance, and materials performance of concrete can have enormous social, economic and environmental impacts [1]. There are a variety of approaches to enhance the sustainability of concrete and reduce its environmental footprint. One of the solutions is to improve the durability of the concrete structures.

Durability of concrete is defined as its ability to resist weathering action, chemical attack abrasion or any other process of deterioration. Durable concrete will retain its original form, quality and serviceability when exposed to its environment [2]. Permeability of concrete is believed to be the major index for this capacity, for it governs the permeation of moisture, ionic, and gaseous species into concrete, and affects durability properties, such as carbonation, sulphate attack, acid attack, corrosion of steel rebar and alkali-aggregate reaction[3].

Carbonation inside concrete is a chemical reaction between carbon dioxide and calcium hydroxide presented in hydrated concrete matrix, which will lower alkalinity of concrete to such an extent that steel embedded may rust and spall the concrete cover. The $CaCO_3$ formed tends to accomodate in the internal pores reducing permeability. Therefore the amount of water contained and the initial porosity of the system undoubtedly has an impact on the rate of the CO_2 diffusion process. Thus the diffusion of CO_2 in water increases. So the rate of carbonation mainly depends on the relative humidity, the concentration of CO_2, the penetration pressure and the temperature of the environment where concrete is placed [3,4].

Resistance of concrete to chloride ingress is a key property for the durability of reinforced concrete structures exposed to deicing salts or sea water.. The extent of chloride attack on reinforced concrete is dependent on the rate of chloride penetration and the corrosion rate of steel reinforcement [5]. The cement hydration leads to the highly alkaline pore solution of concrete, which promotes the formation of an passive film of about 10 nanometres thick at the steel surface. The chloride ions destroy the film, and in the presence of water and oxygen corrosion occurs. The accumulation of corrosion in the concrete pore space near the rebar then builds up hoop stresses around steel and results in cracking or spalling of the concrete, which in turn facilitates the ingress of moisture, oxygen, and chlorides to the embedded rebar and accelerate the corrosion of steel. Corrosion is not a serious issue for concrete but if chloride penetrates into concrete, it can cause fast and severe corrosion of the reinforcement which reduces the cross-section of the reinforcement and thus leads to the loss of its load carrying capacity. [2].

Sulphate attack is the term used to describe a series of chemical reactions between sulphate ions and the components of hardened concrete, principally the cement paste, caused by exposure of concrete to sulphates and moisture [6]. The effects of sulphate attack can be estimated by the loss in strength of the specimen due to degradation of C-S-H gel, by its expansion due to the formation of ettringite, by its loss of mass or even can be assessed visually. Sulphate resistance of the specimen is measured by monitoring the change in compressive strength at 30 to 60 day intervals.

2. CHEMICAL DURABILITY TESTS

The resistance of concrete to durability issues carbonation, chloride attack and sulphate attack can be tested in the laboratory by the following experiments respectively Phenolphthalein test, Rapid chloride ion penetration test and Compressive strength test. In the phenolphthalein test the broken surface will be sprayed with 1% or 2% phenolphthalein solution. . The

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surface where the pH is greater than 9 turns magenta and a gradually lightening shades of pink for pH of 8-9. The location where the surface is colorless represents the depth to which full or nearly full carbonation has been achieved and the pH of the cement is at or below ~8[7].
Bulk diffusion test is carried out in concrete to test the extend of chloride attack in concrete. The samples are split, and the depth of chloride penetration is determined in one half of the specimen using a colorimetric technique in which a silver nitrate solution is used as a colorimetric 13 indicator. When a silver nitrate solution is sprayed on concrete containing chloride ions, a chemical reaction occurs. The chlorides bind with the silver to produce silver chloride, a whitish substance. In the absence of chlorides, the silver instead bonds with the hydroxides present in the concrete, creating a brownish colour to determine the optimum concentration of silver nitrate solution to be used indicates that a 0.1 N solution is suitable and that the colour change border corresponds to the location of a soluble chloride concentration of 0.15 % by weight of cement. It is examined the total chloride contents as well as the soluble chloride percentage and found that this varied depending upon whether the chlorides came from an external source or were present at initial mixing, the w/c ratio of the concrete, and whether a concrete, mortar or paste were used. The soluble chloride percentages were found to remain constant. This depth of penetration can be used to determine a chloride ion diffusion coefficient.

The sulphate resistance of the specimen is measured by monitoring the change in compressive strength at 30 to 60 day intervals. The sulphate resistance test is performed with a concentration of 10 % sulphate solution, in which the solution is periodically exchanged by the new one. Prior to the exposure to the 10 % sulphate solution, the specimens are cured in water at 20^{o}C for 14 days and then stored at 20 ^{o}C for 14 days under a sealed condition. At the age of 28 days, the specimens are immersed completely in the 10% sulphate solution.

The experiments conducted in different locations at different exposure conditions can be normalised by calculating the relative values of test results. In the modelling relative values of carbonation depth, diffusion coefficient and compressive strength is used. The relative carbonation depth is defined as the ratio of carbonation depth of mix with different proportion of cement and fly ash to the carbonation depth of control mix. The relative diffusion coefficient is the ratio of diffusion coefficient of mix with different proportion of cement and fly ash to the diffusion coefficient of control mix. The relative compressive strength is taken as the ratio of compressive strength of blended concrete to the OPC.

3. DATA COLLECTION AND PROCESSING

About 50 papers are selected from the journals published all over the world. All the papers conforms to the standard testing and concrete exposure conditions (list of the literatures are given in APPENDIX). The details collected from the papers include the following

1. Chemical constituents of the binder
2. Percentage of different oxides in each mix
3. Carbonation depth at the age of 28 days
4. Chloride ion diffusion coefficients for each mix at the age of 28 days
5. Compressive strength at the age of 90 days

In every experiment there is a control mix with cement as the binder and all other mixes have both cement and fly ash as binder but in different mix proportions.

3.1 Composition of binder

The binder means both cement and fly ash. The chemical constituents taken into consideration for the study are alumina, silicon dioxide, iron oxide, calcium oxide and sulphur trioxide. Class F fly ash normally produced by burning anthracite or bituminous coal usually has 50% of Silicon dioxide and less than 5% of Calcium oxide (CaO) whereas cement contains a large amount of Calcium oxide (CaO) and a smaller content of silicon dioxide.

3.2 Control ratios

The control of clinker composition and optimisation of cement plant performance is greatly assisted by the use of four ratios Lime saturation factor (LSF), Alumina ratio (AR), Silica ratio (SR) and Hydraulic modulus (HM).

$$LSF = \frac{CaO - 0.7SO_3}{2.8SiO_2 + 1.20Al_2O_3 + 0.65Fe_2O_3} \quad ..(1)$$

$$SR = \frac{SiO_2}{Al_2O_3 + Fe_2O_3} \quad ....(2)$$

$$AR = \frac{Al_2O_3}{Fe_2O_3} \quad ....(3)$$

$$HM = \frac{CaO}{SiO_2 + Al_2O_3 + Fe_2O_3} \quad ....(4)$$

The control ratio LSF, AR, SR and HM are calculated using the percentage of silica, alumina, lime, iron oxide and SO_3. All the calculations are made using Microsoft Office Excel.

4. MODELLING

Regression analysis is used for the purpose of modelling. About 70% of the data is used for the equation formulation and remaining 30% of the values are used for model or equation verification. Two models are developed for each of the durability issue using regression analysis.

1. Model 1: Durability Vs Oxide Composition
2. Model 2: Durability Vs Control ratios

4.1 MODEL-1

In model-1 3 different equations were developed for modelling the durability issues, carbonation, chloride attack and sulphate attack. The input values of the Model 1 include the percentage composition of the chemical components of the binding material like SiO_2(S), Al_2O_3(A), Fe_2O_3(F)and CaO(C). The models are then validated by comparing the model values and actual values for a selected sample. Following are the results of modelling.

4.1 Relative carbonation depth Vs Oxide Composition

$$C_d = 0.01152S + 0.05832A + 0.11912F + 0.000685C \quad \text{......(5)}$$

$R^2 = 0.965$

C_d = Relative carbonation depth

It is observed that all the four constituents has positive effect. The positive effect is mainly due to the pozzolanic activity of the fly ash. Validation of the model is given in figure 4.1.

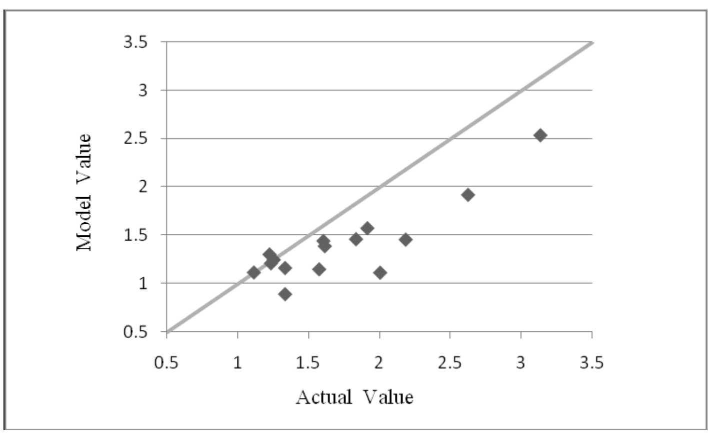


Figure 4.1 Validation of model-I(C_d)

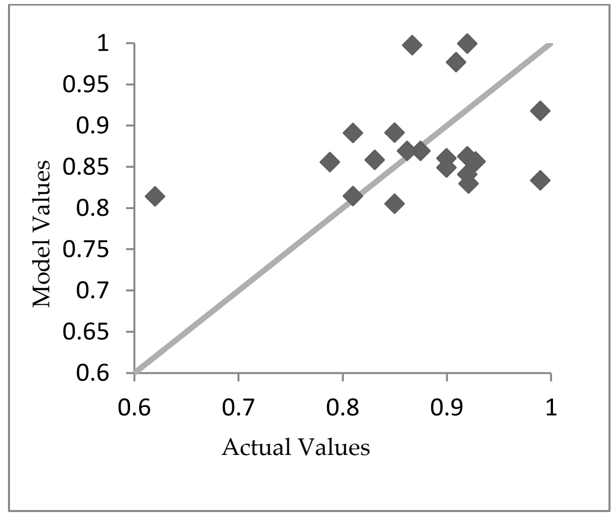
4.1.2 Relative diffusion coefficient and chemical constituents of the binder

$$D = (12686C - 8666S + 44046A + 17542F) \times 10^{-6} \quad \text{..... (6)}$$

$R^2 = 0.96219$

D = Relative diffusion coefficient

From the equations, it is clear that the silica has negative effect on the chloride diffusion coefficient. This is because of the pozzolanic action of the SiO_2. Validation of the model is given in figure 4.2.



4.1.3 Relative compressive strength v/s Oxide composition

$$Y = 0.003996S - 0.00132A + 0.077452F + 0.012229C \quad \text{....(7)}$$

$R^2 = 0.95932$

It can be observed from the equation, that with the increase in Al_2O_3 the relative strength value decreases i.e, it has a negative effect on relative strength. It is also clear that with the increase percentage of SiO_2, Fe_2O_3 and CaO the relative strength value increases i.e, it a positive effect can be observed with all the other oxides.

The negative effect of Al_2O_3 is mainly because the aluminate compounds present in the binding material are affected by sulphates forming a compound called ettringite. The formation of ettringite causes internal pressure which fractures the concrete and reduces the strength. Thus with the increase in Al_2O_3 (%) the chances for the formation of ettringite is more and more chance for reducing the strength.

The positive effect is mainly because of the pozzolanic activity of the fly ash which reduces the formation of gypsum. Fly ash combines with free lime so that it is no longer available for reaction with sulphates. Validation of the model is given in figure 4.3

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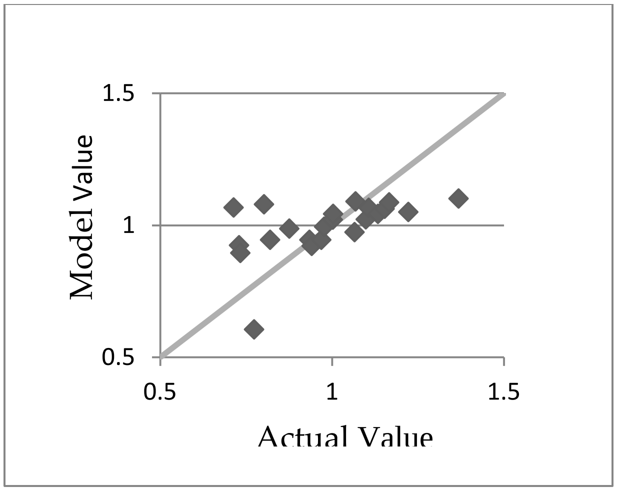

Figure. 4.3 Validation of Model(Y)

From the figures 4.1 4.2 and 4.3 it is clear that majority of the model values falls on the straight line which indicates that model values and actual values are the same. Below the red line it is seen that the models underestimates the relative strength value and above the red line models overestimates the value.

4.2 MODEL-II

The input values of model 2 are control ratios which include Silica ratio, Alumina ratio, Lime saturation factor and Hydraulic modulus. Using regression analysis equations were formulated which connects the relative durability parameter and control ratios.

4.2.1Relative carbonation depth v/s Control ratios

$$C_d = 0.563829SR + 0.05977AR + 9.929874LSF - 4.43137HM \quad ....(8)$$

R^2=0.984

It is clear from the equation that HM ratio has a negative effect on the relative carbonation depth i.e, as the carbonation depth increases, HM decreases. Hence it gives resistance to chemical attack. Validation of the model is given in figure 4.4

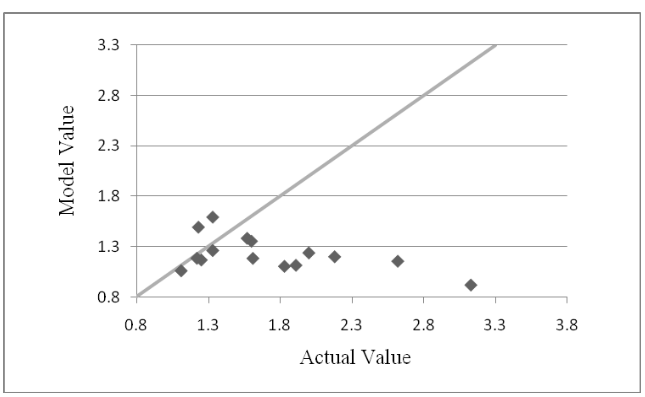

Figure 4.4 Validation of model-II (C_d)

4.2.2 Relative diffusion coefficient Vs Control ratios

$$D = 0.2548SR + 0.677755AR + 6.73129LSF - 2.88283HM \quad ....(9)$$

R^2= 0.954921

D = Relative diffusion coefficient

Validation of the model is given in figure 4.5.

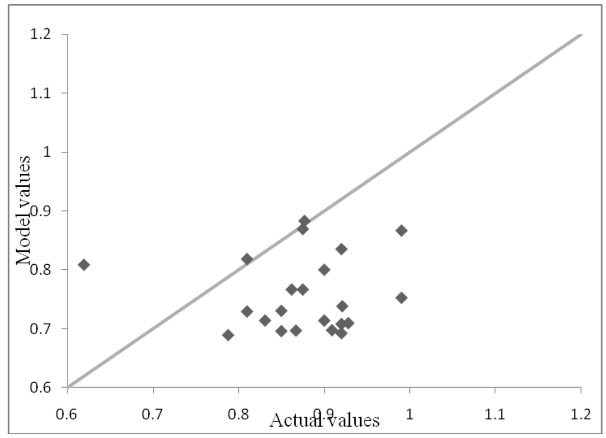

Figure. 4.5 Validation of model 2 (D)

4.2.3 Relative compressive strength vs Control ratios

Y = 0.441163 SR - 0.00861AR + 10.4585 LSF - 4.45657 HM..(10)
R^2=0.949774

It is clear from the equation that, the ratio SR has a positive effect on the relative strength value i.e, as SiO_2 increases of Al_2O_3/Fe_2O_3 decreases the relative strength value increases. The ratio AR has a negative effect on the relative strength as Al_2O_3 increases or Fe_2O_3 decreases the relative strength decreases. The ratio LSF has a positive effect and is the most important ratio in determining the relative strength i.e, with the increase in Cao and with the decrease in SO_3 the relative strength increases. The ratio HM is observed to have a negative effect on strength. Validation of the model is given in figure 4.6.

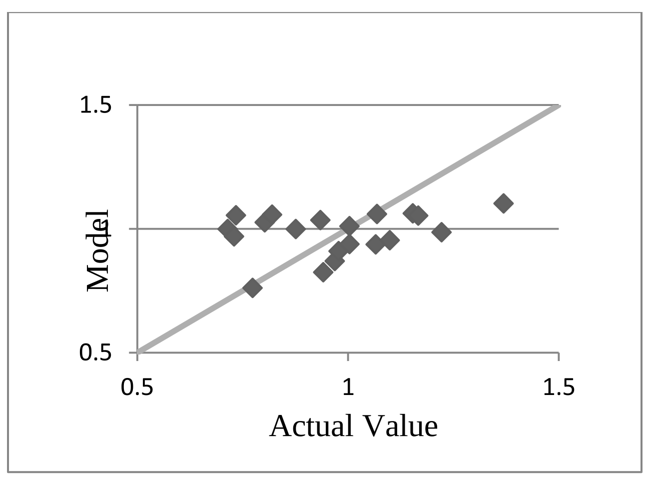

Figure. 4.6 Validation of model 2 (Y)

From the figures 4.4, 4.5 and 4.6 it is clear that below the straight line models underestimates the relative strength value and above the red line the model overestimates the value.

5 CONCLUSION

In this project the author analysed various durability issues in fly ash blended concrete. The multiple regression analysis is used for the development of equations connecting the relative durability parameter, and chemical constituents of the binder and the control oxide ratios in the binder. Using the suggested models, it is possible to estimate the relative chloride diffusion coefficient, relative carbonation depth and relative compressive strength of concrete containing fly ash as the supplementary cementitious material, if the oxide composition of the binder system is known.

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