

CHLORIDE DIFFUSION COEFFICIENT IN FULLY SATURATED CONDITIONED CONCRETE CUBES

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Abstract: The concrete is strong in compression but weak in tension, versatile, and brittle material which is serving from so many decades for construction industries all over the world. The successful key for making durable concrete is to limit its ability to transport fluids like water. In order to devise realistic testing methods, that determine the ability of concrete to withstand water penetration requires an understanding of water mobility. In order to build durable oriented and practicable concrete structures, it is needed to be able to accurately predict the chloride diffusion coefficient the within concrete structures. Therefore, there is a need to quantify the chloride diffusion coefficient in concrete cubes which is of most important factor. The present research work is made an attempt to interpret the concrete chloride diffusion coefficient in ordered to characterize the different concrete mixtures design for in case of concrete cubes. Thus the objectives of this present research are such as, First, this research will examine the influence of concrete ingredients on the results of chloride diffusion coefficient performed on concrete cubes with different mixtures proportion in which slump, and w/c ratio value is varied with constant compressive strength as in the first case and compressive strength, and w/c ratio value varied with constant slump as in the second case. Seventy-two concrete cubes (100 mm³) with grades of concrete ranges from 25-40 N/mm² were prepared and evaluate the chloride diffusion coefficient under different at different time interval. The chloride diffusion coefficient is co-related with square root of time by power type of equation for in case of control/impregnation concrete cubes in all designed concrete mixtures type. Chloride diffusion coefficient is increased with centration gradient at an initial time duration as when compared to longer time duration for in case of designed mixtures type. The chloride diffusion coefficient is increased with square root of time for in case of water based impregnation concrete cubes as when compared to solvent based impregnation concrete cubes. It's also confirmed from the results that, chloride diffusion coefficient is slightly higher for in case of control concrete cubes as when compared to impregnation concrete cubes for in case of solvent/water based impregnation concrete cubes.

Keywords: Concrete, mixture proportion, grade of concrete, w/c ratio, chloride diffusion coefficient, slump, impregnation

1.0 Introduction

The corrosion rate is controlled by many factors such as total chloride ion content of the pore solution, pH level, and availability of oxygen, water content, and temperature. In corrosion decay of steel in concrete several processes may be combined, making it difficult to identify a single mechanism. One of the mechanisms for surface penetration is intrusion of chloride-bearing water into capillary pores of unsaturated concrete by capillary action. Alternate wetting/drying can lead to build up of chloride ions through absorption. If a structure is not dried to a high degree for prolonged period of time, chloride penetration into concrete by absorption and capillary suction is basically restricted to a small depth below the surface. If there is a differential head of chloride bearing water, permeability will also influence the ingress of chlorides for which higher permeability coefficient will permit higher rate of flow. The other dominant mechanism of the chloride ion transport is the diffusion which takes place under a concentration gradient. If outside concentration is higher than the inside of concrete, the migration of chloride ions through pore water in concrete will take place by diffusion. The relative importance of the two major mechanisms of chloride transport, namely diffusion and absorption, depend on the moisture content of concrete. Absorption may be dominant if a dry concrete with significant loss of pore water is wetted with chloride-bearing water, whereas for a reasonably moist concrete (sufficient level of pore water exists) diffusion process will prevail. However, researchers tend to agree that in most cases diffusion can be assumed to be the basic transport mechanism of chloride ions for reasonably moist structures. Experimental and analytical studies are carried out to predict the ingress of chloride ions in partially and fully saturated concretes. Models incorporating chloride dispersion, advection and adsorption with and without water diffusion, sorptivity and permeability, together with appropriate initial and boundary conditions, are proposed. The rate of chloride ingress, as represented by the depth of chloride penetration, is dependent on w/c ratio, chloride concentration of immersion solution, water content, applied

hydrostatic pressure gradient, exposure period and surrounding conditions. Within the experimental limits of this study, the ionic chloride diffusion coefficient decreases with lower water content, but is not significantly affected by the external chloride concentration. Improvement in the resistance to chloride ingress with and without water movement can be achieved by selecting OPC concretes of a lower water-cement ratio, possibly due to greater micro structural densification [Swaddiwudhipong, *et al*, 2000]. The corrosion of reinforcing steel due to chloride ions is one of the severe deterioration problems in long term performance of reinforced concrete structures. Chloride penetration into concrete structures was mathematically characterized by the Nernst-Planck equation which considered not only diffusion mechanism of the chloride ions but also ionic interaction among other ions coming from externally applied de-icers and within the Portland cement paste. A numerical example was used to illustrate the coupling effect of multi-ionic interactions and the effect of influential parameters and numerical results obtained from the present model agreed very well with available test data [Nattapong Damrongwiriyapap, *et al*, 2011]. The diffusion of hydrated chlorine ions (Cl^-) in concrete is influenced by the porosity and the composition of hardened cement paste. Results of the experimental series demonstrate that the addition of aluminates, granulated blast furnace slag or fly ash to ordinary Portland cement considerably reduces the diffusion rate of Cl^- . The reduction of the diffusion rate depends not only on the amount and the chemical composition of the additives but also on their mineralogical structure. All these factors are incorporated in the presented mathematical formulation of the Cl^- diffusion coefficient [Frey, *et al*, 1994]. Saetta *et al.* modeled the diffusion of Cl^- in partially saturated concrete by considering the flows of moisture, heat and Cl^- through a porous medium. The simulation simulation of chloride penetration in saturated concrete has also been conducted [Xi, and Bazant, 1999], in which two models are developed for chloride binding capacity and diffusivity. On the other hand, a micro structural model has been established [Garboczi, and Bentz, 1998], taking into account the effect of redistribution of cement paste between the interfacial transition zone and bulk paste on the chloride diffusivity of concrete. Based on effective media theory, a predictive model, relating chloride diffusivity to the capillary pores, gel pores, tortuosity factor, and pore size distribution of hardened cement, is proposed. The predicted results for chloride diffusivity were compared with published data. The results showed that the predicted chloride diffusivity of hardened cement paste was in good agreement with the experimental results. The effect of the evolution of pore structures in cement paste on chloride diffusivity could be deduced simultaneously using the proposed model [Guo-wen Sun, *et al*, 2011].

The concrete durability is dependent on mechanism of moisture transport within the concrete matrix. The moisture transport is occurred in marine environment, where drying and wetting cycles occur, which leads chloride to penetrate into reinforced concrete structures. In fact that, when chloride reaches the rebars, corrosion can appear and that decreases the service life time of the concrete structures. Actually so many descriptions about moisture transport in concrete can be found in the literature such as the authors [Arfvidsson, 1999] describe moisture transport in concrete structures by using a single diffusion coefficient. The moisture diffusion factor is very the long term duration performance of cementitious materials which is described by so many diffusion equations as well as solved by numerous numerical methods if provided the coefficients are well known. However, there is a need to investigate about diffusion coefficient and transport behavior of the materials which is still remain an unsolved problem even though many different models have been proposed [Bazant, and Najjar, 1972]. There is a major difficulty in establishing reliable diffusion parameters, because diffusion of moisture inside cementitious materials is basically controlled by the micro-structure of the material, and pore-size distribution. In fact that, the microstructure is changing with age as well as with relative humidity in the pores. Therefore, all of the parameters, such as the water/cement ratio, type of cement, and curing time, which affect the formation of the microstructure of cementitious materials, thus have significant effects on diffusion parameters. The water movement is very slow in the concrete in turn it takes too much time to attain the equilibrium state as when compared to other porous materials and the study of water movement is firstly done by [Sakata, 1983]. He is the one who is used Boltzmann-Matano method other methods, in fact that, Boltzmann-Matano method has a benefit regarding cement based material research. Also an extensive research is carried out by [Akita and Fujiwara, 1990] on the water movement. They used different approaches to obtain the relationship between water content and water diffusion coefficient, and obtained consistent results to those by [Sakata, 1983]. In addition to these results that, they found the temperature dependency of water diffusion coefficient, water diffusion coefficient in very low water content region, and water diffusion coefficient of desorption and adsorption processes. An improved formula for the dependence of diffusivity on pore humidity is proposed by [Yunping Xi, *et al*, 1994].

The improved model for moisture diffusion is found to give satisfactory diffusion profiles and long-term drying predictions. The model is suited for incorporation into finite element programs for shrinkage and creep effects in concrete structures. An extensive research is carried out by researchers [Rafik Belarbi, *et al*, 2006] that, gravimetric method is adopted for the determination of moisture diffusion coefficient and moisture distribution inside porous building materials. It's confirmed from the results that, the moisture diffusion coefficient during absorption is higher than desorption process due to the absorption hysteresis, an increase of water-cement ratio in cement paste. The high-strength concrete has a lower moisture diffusion coefficient than that of normal strength concrete under the same curing period. An experimental work is carried out by [Su-Tae Kang, *et al*, 2012] on moisture diffusion in order to investigate the variation of the moisture diffusion coefficient with age

and temperature under different temperature conditions. Based on these experimental results, it's possible to develop a new model of the moisture diffusion coefficient considering the aging and temperature which is implemented by a numerical inverse analysis. As this model is considers factors such as porosity, humidity, and temperature, beyond the existing model for hardened concrete, and the suggested diffusion coefficient model is applicable to early age concrete. The investigation about the moisture transport mechanisms in concrete is important in order to determine the service life of a concrete structure. In fact so many authors were managed to describe the global moisture transport mechanisms in concrete structures during wetting/drying cycles by using Fick's laws of diffusion. An extensive comparison is made between the results of a model with two diffusion coefficients and a model with a single diffusion coefficient, where the diffusion coefficient is the average of the wetting and drying diffusion coefficient by investigators [Taher, *et al*, 2013]. The result is computed for one cycle of wetting and drying and simulations show that, there are differences in the results of the models. In order to validate the model and to investigate which of the models describes the moisture transport most accurately, in fact that, there is an extensive experimental work is needed. The research work is carried out by investigators [Xiao Zhang, *et al*, 2015] that, in order to investigate the characterization of moisture diffusion inside early-age concrete slabs subjected to curing and in which time-dependent relative humidity distributions of three mixture proportions subjected to three different curing methods and sealed condition were measured for about 28 days. Experimental results show that the RH reducing rate inside concrete under air curing is greater than the rates under membrane-forming compound curing and water curing. In addition to that, the comparison between model simulation and experimental results indicates that, the improved model is able to reflect the effect of curing on moisture diffusion in early-age concrete slabs.

2.0 Research Objectives

The chloride transport in a porous network like concrete is a complex criterion. This is due to the fact that, many different kinds of transport mechanisms in combination with various types of pores that typically appears in the same porous system. Therefore there is a need to study chloride transport mechanisms with different designed mixtures type in order to assess the rate of chloride diffusion coefficient in concrete structures. The present research work is made an attempt to interpret the concrete chloride diffusion coefficient in ordered to characterize the different concrete mixtures design for in case of concrete cubes. Thus the objectives of this present research is to examine the influence of concrete ingredients on the results of concrete chloride diffusion coefficient in concrete cubes with different mixtures proportion in which slump, and w/c ratio value is varied with constant compressive strength as in the first case and compressive strength, and w/c ratio value varied with constant slump as in the second case. Seventy-two concrete cubes (100 mm³) with grades of concrete ranges from 25-40 N/mm² were prepared and evaluate the concrete chloride diffusion coefficient in concrete cubes.

3.0 Experimental program

In the present research work, six different mixtures type were prepared in total as per [BRE, 1988] code standards with concrete cubes of size (100 mm³). Three of the mixtures type were concrete cubes (100 mm³) with a compressive strength 40 N/mm², slump (0-10, 10-30, and 60-180 mm), and different w/c (0.45, 0.44, and 0.43). These mixtures were designated as M1, M2, and M3. Another Three of the mixtures type were concrete cubes with a compressive strength (25 N/mm², 30 N/mm², and 40 N/mm²), slump (10-30 mm), and different w/c (0.5 0.45, and 0.44). These mixtures were designated as M4, M5, and M6. The overall details of the mixture proportions were to be represented in Table.1-2. Twelve concrete cubes of size (100 mm³) were cast for each mixture and overall Seventy-two concrete cubes were casted for six types of concrete mixture. The coarse aggregate used is crushed stone with maximum nominal size of 10 mm with grade of cement 42.5 N/mm² and fine aggregate used was 4.75 mm sieve size down 600 microns for this research work. As concern to impregnation materials, Water based (WB) and Solvent based (SB) impregnate materials were used in this present research work. To avoid criticizing or promoting one particular brand of impregnation materials and for confidentiality reasons, the names of the products used will not be disclosed and they will be referred to as WB and SB respectively. WB is water borne acrylic co-polymer based impregnation material which is less hazardous and environmental friendly. It is silicone and solvent free and achieves a penetration of less than 10mm. SB consists of a colourless silane with an active content greater than 80% and can achieve penetration greater than 10mm.

Table: 1 (Variable: Slump & W/C value; Constant: Compressive strength)

Mix No	Comp/mean target strength(N/mm ²)	Slump (mm)	w/c	C (Kg)	W (Kg)	FA (Kg)	CA(Kg) 10 mm	Mixture Proportions
M1	40/47.84	0-10	0.45	3.60	1.62	5.86	18.60	1:1.63:5.16
M2	40/47.84	10-30	0.44	4.35	1.92	5.62	16.88	1:1.29:3.87
M3	40/47.84	60-180	0.43	5.43	2.34	6.42	14.30	1:1.18:2.63

Table: 2 (Variable: Compressive strength & W/C value; Constant: Slump)

Mix No	Comp/mean target strength(N/mm ²)	Slump (mm)	w/c	C (Kg)	W (Kg)	FA (Kg)	CA(Kg) 10 mm	Mixture Proportions
M4	25/32.84	10-30	0.50	3.84	1.92	5.98	17.04	1:1.55:4.44
M5	30/37.84	10-30	0.45	4.27	1.92	6.09	16.50	1:1.42:3.86
M6	40/47.84	10-30	0.44	4.35	1.92	5.62	16.88	1:1.29:3.87

3.1 Chloride diffusion coefficient

The chloride diffusion coefficient is determined from the solution of one-dimensional Fick's theory for unsteady diffusion process. The percent of chloride solution absorption gain at any time t , (M_t) can obtain from the solution of the one-dimensional Fick's model with constant boundary conditions as:

$$M_t = M_{\infty} \left[1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} (2n+1)^{-2} \exp\left[-\frac{D(2n+1)^2 \pi^2 t}{L^2}\right] \right]$$

Where M_{∞} is the chloride solution absorption gain at saturation equilibrium (%), n is a known integer which is varied from material to material, L is the thickness of the material, and D is the diffusivity of the material. At initial stages of diffusion, the solution for Fick's law at lesser time reduces to as:

$$\frac{M_t}{M_{\infty}} = 4 \sqrt{\left(\frac{D}{\pi L^2}\right) t}$$

It's also possible within this present research work that, to interpret the chloride diffusion coefficient in pre-conditioned control FSC (M1CC-M6CC) and impregnation concrete cubes (M1SB-M6SB/M1WB-M6WB) on the basis of chloride solution absorption at different specified time intervals (1, 3, 6, 9, 12, 15, 18, 21, and 24 days) with their varied chloride diffusion coefficients in FSC cubes as represented in the Table.3.

Table: 3 Chloride diffusion coefficient in FSC/SB/WB concrete cubes

Mix ID	1 day	3 day	6 day	9 day	12 day	15 day	18 day	21 day	24 day
M1CC	1.0787	0.8198	0.6699	0.6232	0.5800	0.5487	0.5243	0.5045	0.4881
M1SB	1.0795	0.8203	0.6413	0.6233	0.5803	0.5489	0.5245	0.5047	0.4881
M1WB	1.0785	0.8196	0.6534	0.6232	0.5800	0.5485	0.5241	0.5042	0.4881
M2CC	1.0736	0.8158	0.6688	0.6200	0.5770	0.5457	0.5214	0.5020	0.4882
M2SB	1.0763	0.8190	0.6544	0.6226	0.5795	0.5482	0.5239	0.5042	0.4880
M2WB	1.0782	0.8193	0.6529	0.6226	0.5794	0.5480	0.5241	0.5043	0.4877
M3CC	1.0787	0.8197	0.6593	0.6230	0.5799	0.5485	0.5241	0.5043	0.4878
M3SB	1.0801	0.8208	0.6692	0.6237	0.5804	0.5489	0.5245	0.5047	0.4881
M3WB	0.8833	0.6712	0.6664	0.5102	0.4748	0.4491	0.4291	0.4129	0.3996
M4CC	0.9903	0.7531	0.6564	0.5731	0.5336	0.5047	0.4822	0.4640	0.4489
M4SB	1.0793	0.8202	0.6713	0.6232	0.5800	0.5485	0.5241	0.5043	0.4881
M4WB	1.0795	0.8203	0.7009	0.6234	0.5802	0.5487	0.5244	0.5047	0.4881
M5CC	1.0291	0.7821	0.6728	0.5944	0.5532	0.5232	0.4999	0.4820	0.4708
M5SB	1.0793	0.8201	0.7734	0.6232	0.5801	0.5486	0.5242	0.5045	0.4881
M5WB	0.9924	0.7541	0.6287	0.5732	0.5334	0.5045	0.4821	0.4639	0.4538
M6CC	1.0634	0.8080	0.6632	0.6140	0.5714	0.5404	0.5168	0.4973	0.4814
M6SB	1.0772	0.8193	0.5934	0.6232	0.5799	0.5485	0.5240	0.5042	0.4882
M6WB	1.0585	0.8044	0.6450	0.6112	0.5688	0.5379	0.5142	0.4948	0.4786

4.0 Discussion about Results

The chloride diffusion coefficient is gradually increased at initial time duration, afterwards deviates with square root of time duration and reaches equilibrium in turn indicates that, pore structure is attained fully saturated condition. The chloride diffusion coefficient is increased at time interval (2.23 min) as when compared to time interval (173.89 min) for in case of all designed control mixtures type [(M1CC-M2CC:0.39-0.49, M1CC-M3CC:0.32-0.03, M1CC-M4CC:9.38-8.02, M1CC-M5CC:5.57-4.45, M1CC-M6CC:2.06-1.42, M2CC-M3CC:-0.07-(-0.46), M2CC-M4CC:9.22-7.57, M2CC-M5CC:5.20-3.98, M2CC-M6CC:1.68-0.94, M3CC-M4CC:9.29-8.00, M3CC-M5CC:5.27-4.42, M3CC-M6CC:1.75-1.39, M4CC-M5CC:-4.43-(-3.89), M4CC-M6CC:-8.31-(-7.18), and M5CC-M6CC:-3.71-(-3.17)]%. The diffusion coefficient is initially increased, in turn due to concentration gradient. Concentration gradient is more at an initial time duration, due to that the rate of absorption is also more, once the pore structure is fully saturated, the rate of diffusion coefficient goes on decreases with time duration. Thus the concentration gradient is more at an initial stage, goes on decreases as time passes and thus diffusion coefficient is reduced gradually as time in turn reaches equilibrium state. The variation of chloride diffusion coefficient in control concrete cubes for in different mixtures type (M1CC-M6CC) is as shown in Figs.1a-1f respectively. Chloride diffusion coefficient is correlated with square root of time by power type of equation for in all designed control mixtures type (M1CC-M6CC).

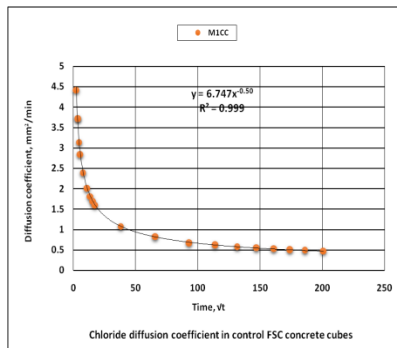


Fig.1a Cl- diffusion coefficient in mix M1

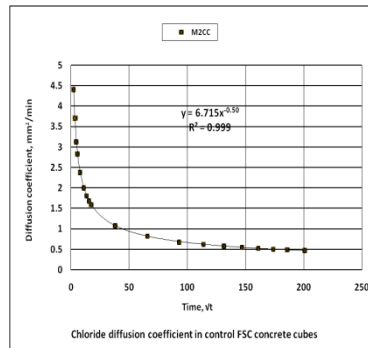


Fig.1b Cl- diffusion coefficient in mix M2

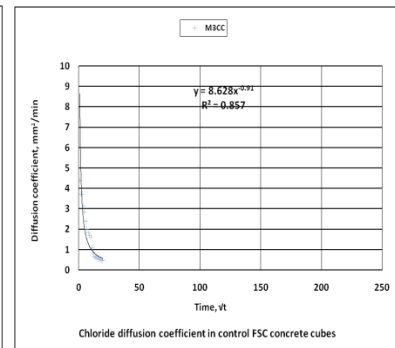


Fig.1c Cl- diffusion coefficient in mix M3

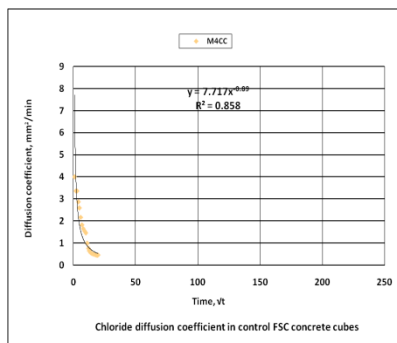


Fig.1d Cl- diffusion coefficient in mix M4

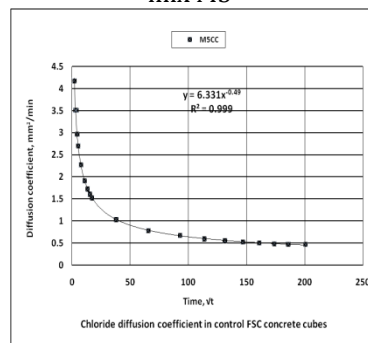


Fig.1e Cl- diffusion coefficient in mix M5

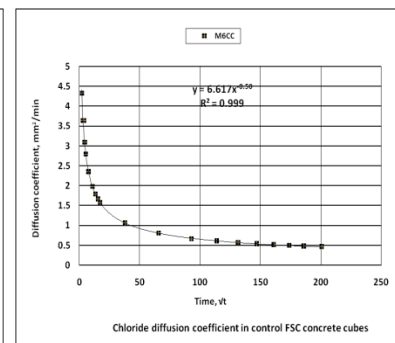


Fig.1f Cl- diffusion coefficient in mix M6

The chloride diffusion coefficient is increased at initial time duration, deviates with square root of time duration and reaches equilibrium when the concrete structure is attained fully saturated condition. The chloride diffusion coefficient is increased at time interval (2.23 min) as when compared to time interval (173.89 min) for in case of all designed control mixtures type as when compared to impregnation concrete cubes [(M1CC-M1SB:0.12-(-0.04), M1CC-M1WB:0.2-0.05, M2CC-M2SB:1.06-(-0.45), M2CC-M2WB:-0.16-(-0.45), M3CC-M3SB:-0.23-(-0.07), M3CC-M3WB:18.44-18.13, M4CC-M4SB:-9.67-(-8.68), M4CC-M4WB:-10.00-(-8.76), M5CC-M5SB:-5.33-(-4.65), M5CC-M5WB:3.36-3.76, M6CC-M6SB:-1.90-(-1.39), M6CC-M6WB:0.41-0.50, and M1WB-M1SB:-0.08-(-0.08), M2WB-M2SB:1.21-0.00, and M3WB-M3SB:-22.89-(-22.23), M4WB-M4SB: 0.30-0.08, M5WB-M5SB:-8.99-(-8.74), M6WB-M6SB:-2.32-(-1.90)]%. The diffusion coefficient is initially increased which may be due to concentration gradient. Variation of chloride diffusion coefficient in impregnation concrete cubes for in case of different mixture type (M1SB-M6SB) is as shown in Figs.2a-2f respectively. Chloride diffusion coefficient is directly correlated to the square root of time by power type of equation in all designed impregnation mixtures type (M1SB-M6SB).

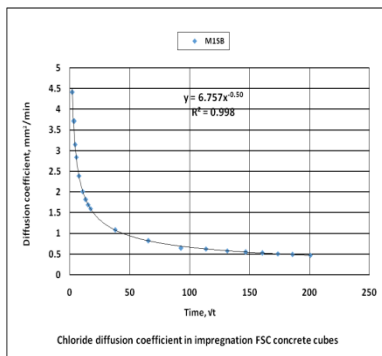


Fig.2a Cl- diffusion coefficient in mix M1

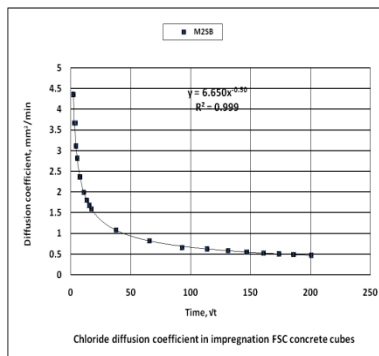


Fig.2b Cl- diffusion coefficient in mix M2

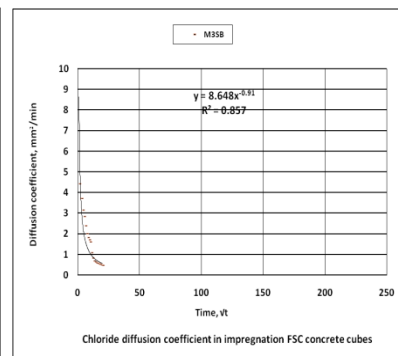


Fig.2c Cl- diffusion coefficient in mix M3

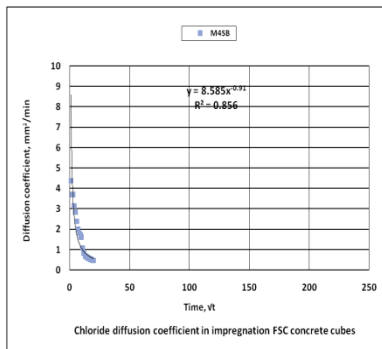


Fig.2d Cl- diffusion coefficient in mix M4

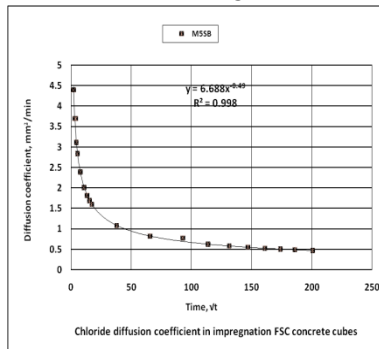


Fig.2e Cl- diffusion coefficient in mix M5

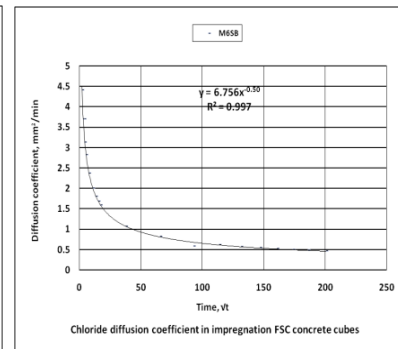


Fig.2f Cl- diffusion coefficient in mix M6

The chloride diffusion coefficient is increased at time interval (2.23 min) as when compared to time interval (173.89 min) for in case of all designed impregnation mixtures type as when compared to different designed impregnation mixture type [(M1WB-M2WB:0.08-0.00, M1WB-M3WB:18.53-18.12, M1WB-M4WB:0.33-(-0.08), M1WB-M5WB:8.55-8.00, M1WB-M6WB:2.26-1.87, M2WB-M3WB:18.50-18.12, M2WB-M4WB:0.30-(-0.08), M2WB-M5WB:8.53-8.00, M2WB-M6WB:2.24-1.87, M3WB-M4WB:-22.33-(-23.23), M3WB-M5WB:-12.24-(-12.36), M3WB-M6WB:-19.96-(-19.85), and M4WB-M6WB:8.25-8.07, M4WB-M6WB:1.94-1.95, and M5WB-M6WB:-6.88-(-6.66)]%. The diffusion coefficient is initially increased which may be due to concentration gradient. Variation of chloride diffusion coefficient in impregnation concrete cubes for in case of different mixture type (M1WB-M6WB) is as shown in Figs.3a-3f respectively. Chloride diffusion coefficient is directly correlated to the square root of time by power type of equation in all designed impregnation mixtures type (M1WB-M6WB).

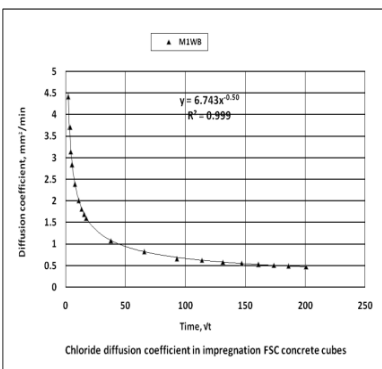


Fig.3a Cl- diffusion coefficient in mix M1

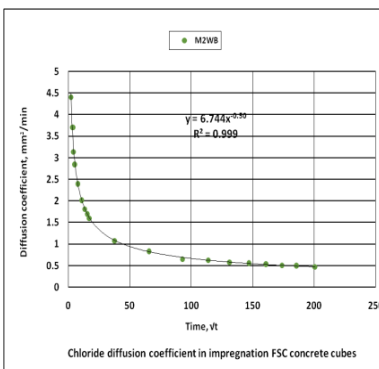


Fig.3b Cl- diffusion coefficient in mix M2

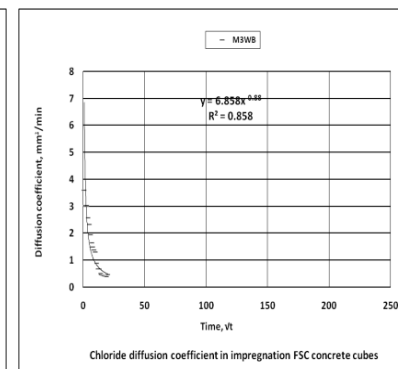


Fig.3c Cl- diffusion coefficient in mix M3

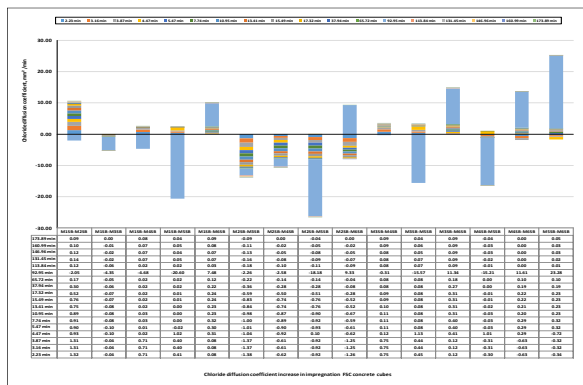


Fig.4c Cl- diffusion coefficient in IC concrete cubes

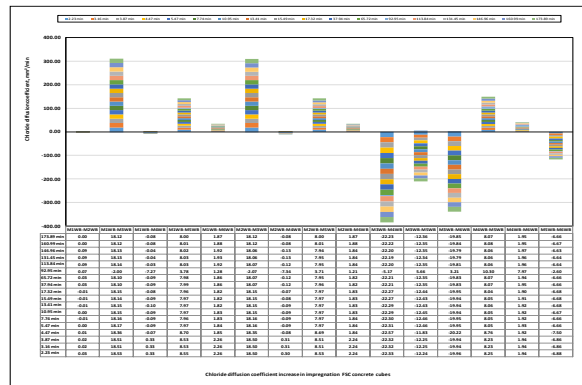


Fig.4d Cl- diffusion coefficient in IC concrete cubes

Chloride diffusion coefficient was also interpreted at different time duration in this present research work for in the case of designed control concrete cubes (M1CC-M6CC) and compared impregnation concrete cubes (M1SB-M6SB, M1WB-M6WB) which is represented as shown in Fig.4e at different time duration (2.23 min) up to time interval (173.89 min) for in case of designed concrete mixtures type.

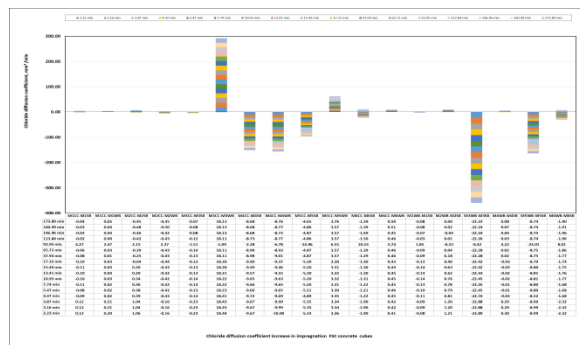


Fig.4e Cl- diffusion coefficient in control/IC concrete cubes

5.0 Conclusions

- The chloride diffusion coefficient is co-related with square root of time by power type of equation for in case of control/impregnation concrete cubes in all designed concrete mixtures type. Chloride diffusion coefficient is increased with concentration gradient at an initial time duration as when compared to longer time duration for in case of designed concrete mixtures type.
- The chloride diffusion coefficient is increased with square root of time for in case of water based impregnation concrete cubes as when compared to solvent based impregnation concrete cubes.
- It's also confirmed from the results that, chloride diffusion coefficient is slightly higher for in case of control concrete cubes as when compared to impregnation concrete cubes for in case of solvent/water based impregnation concrete cubes.

6.0 References

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