Chloride Durability of Supplementary Cementitious Materials – An Electro Chemical Experimental Study

Syed Jamal Uddin Ahmed[1]

Abstract: *This paper describes how supplementary cementitious materials are resistant to chloride ingress when the concrete specimens were subjected to electro-chemical rapid chloride migration tests of two different kinds, namely, Potential Difference (PD) and Multi-Regime (MR) tests. Both the tests measure chloride durability in terms of D, the Coefficient of Chloride Diffusion. The concrete specimens were prepared with Portland cement partially replaced with fly ash, Ground Granulated Blast-furnace Slag (GGBS) and limestone filler and with varying w/c ratio. The PD and MR test results show that in the early ages, 100% Portland cement concrete performed well against chloride diffusion. However, fly ash and GGBS concrete showed higher resistance against chloride migration at later stage. At equal strength grade, w/c ratio and age, GGBS concrete had the highest resistance against chloride among other cement types.*

Keywords: Supplementary Cement, Chloride Ingress

1. INTRODUCTION

Over the decades, concrete has been the most popular construction material around the world for its versatility in terms of strength, durability and moldability. When accompanied by embedded steel, concrete can serve almost any structural purpose. However, corrosion of steel due to ingress of aggressive agents, such as chloride, into concrete has several adverse effects including spalling of surface, reduction in cross-sectional area, disintegration and total structural failure. Concrete structures that have been built in corrosive environment start deterioration well before their design life end [1]. Coastal and marine concrete structures are highly exposed to chloride intrusion. Highway structures are also subjected to chloride attack where de-icing salt is applied in cold weather countries. Recent developments in the research of supplementary cementitious materials have already established the standards for structural performance; however, researchers have been

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[1] Lecturer, UITS.

continuing there investigation for the optimum durability performance of supplementary cementitious materials. This paper studied the chloride durability of supplementary cementitious materials by rapid chloride migration method.

1.1 Supplementary Cementitious Materials

Although modern Portland cements have much improved properties, its production is highly energy-intensive and responsible for significant amount of carbon-dioxide gas emission. Global yearly production of Portland cement accounts for 7% carbon-dioxide gas release into the atmosphere while each ton of production requires 4GJ of energy [2]. It has already been established that utilization of supplementary cementitious materials, which are by-products of other processes, has sustainably improved the cement and concrete industries by reducing environmental impacts associated with cement production [3]. Fly ash and Ground Granulated Blust-furnace Slag (GGBS) are the examples of such materials produced by thermal power plants and metallurgical industries.

Addition of fly ash and GGBS has been reportedly popular means of resisting chloride intrusion into concrete among majority in the researchers' community. Inclusion of these cements tends to reduce chloride permeability and risk of corrosion in turn. The improvement has been associated with a number of physical and chemical properties of these materials, resulting in changes in both pore chemistry and microstructure. Pozzolanic properties of these supplementary cementitious materials impart dense microstructure into concrete which is beneficial against chloride ion ingress [4]. In addition to this, nature of the capillary pore system, secondary hydration reaction and chloride binding capacity of pozzolanic materials significantly increase the chloride resistivity of concrete [5].

1.2 Measurement of Chloride Resistance

Based on the mechanism of natural chloride diffusion and rapid electrochemical migration of chloride ions a number of test methods have been developed in order to measure chloride diffusion into concrete specimens. In practice, all these tests measure the coefficient of diffusion, *D* or equivalent, which is often used as a fundamental parameter to describe the ease with which chloride is transported through concrete. A number of natural diffusion test have been proposed by several researchers. Concentration difference method (CD) was proposed by Dhir *et al.* [6] that determines the diffusion of chloride in the steady-state condition. Andrade *et al.* [7] proposed a ponding test as a comparative test to compare diffusivity value for accelerated migration test. This test takes one year to complete. Nordtest NT BUILD 443 was proposed as part of the 'chlortest research project' to evaluate the resistance of concrete against chloride penetration. It is based on a bulk diffusion test running for about 90 days with 30 days preconditioning.

Since testing of 'natural' chloride penetration is time consuming, attempts have been made to calculate the coefficient of diffusion, D by accelerating the rate of penetration of chloride ions with the application of electrical field [8]. Since 1980s, rapid test for chloride diffusion has been made possible by the standardisation of a test method by Whiting [9] in the ASTM. Several researchers proposed what can be called as migration type tests based on the two cell test principles. Among others who proposed similar test methods are Dhir *et al.* [6], Tang and Nilsson [10], Andrade *et al.* [7, 8, 11] and others [12-15]. The test methods adopted in this study are PD test and Multi-Regime Test developed respectively by Dhir *et al.* (1990) and Andrade *et al.* [8, 11].

2. EXPERIMENTAL PROGRAM

The experimental programme considered comparative study on different cement types, therefore alternative cements including Fly Ash, GGBS and limestone filler were introduced as partial replacement of Portland cement. The chemical and physical properties of Portland cement and other supplementary cementitious materials as determined by quantitative X-ray diffraction technology are provided in Table 2.1.

The mix proportions were adopted from the basis of the minimum requirement from the British Standard, BS 8500-1 [16] for XD3 class which is stated as the most severe chloride exposure class with cyclic wet and dry environmental condition. Mix proportion is shown in Table 2.2.

Table 2.1 Chemical composition of cements determined by X-ray Diffraction

a. Oxides Composition, %	Cement and addition types			
	PC	Fly ash	GGBS	Limestone
CaO	65.17	3.56	40.18	81.55
SiO_2	20.68	45.9	35.02	0.11
Al_2O_3	5.17	21.05	11.83	0.06
Fe_2O_3	2.97	10.05	0.43	0.02
MgO	1.02	1.406	7.272	0.167
MnO	0.047	0.081	0.533	0.027
TiO_2	0.496	1.118	0.67	-
K_2O	0.576	2.811	0.569	0.003
Na_2O	0.304	1.271	0.31	0.072
P_2O_5	0.219	0.448	0.015	0.014
Cl	0.027	0	0	0
SO_3	3.011	1.256	1.031	0.027

Table 2.2 Constituents proportion adopted from BS-8500

Proportion & Designation	Constituents Material (kg/m³)								
	Cements						Aggregates		
	w/c ratio	PC	GGBS	Fly Ash	Limestone	Total Cement	Fine	10/4 mm	20/10 mm
100% PC M1	0.35	380				380	736	403	748
	0.40	380				380	729	399	740
	0.45	360				360	732	401	745
70% PC 30% FA M2	0.35	266		114		380	716	392	729
	0.45	252		108		360	713	390	725
	0.55	224		96	10	330	707	396	735
30% PC 70% GGBS M3	0.40	114	266			380	725	397	736
	0.50	102	238			340	733	401	746
	0.55	96	224		10	330	723	404	751
85% PC 15% Limestone M4	0.35	323			57	380	736	403	748
	0.40	323			57	380	729	399	740
	0.45	306			54	360	732	401	745

The mixing was carried out in accordance with British Standard BS 1881-125: 1986 in a horizontal pan type mixer. Properties of fresh and hardened concrete i.e. slump and compressive strength are shown in

Table 2.3. Workability of concrete mixes was measured in terms of slump in accordance with the description provided in BS EN 12350-2: 2009

General trend of strength development for all cement types are similar, i.e. compressive strength increased with time. Decrease in w/c ratio also showed increase in strength as usual. However, trends of strength development of Fly Ash and GGBS concrete suggest that these concrete types will gain similar or higher strength at their later age due to slow and continued hydration.

Table 2.3 Slump values and strength development

Proportion & Designation	Concrete properties				
	w/c ratio	Achieved Slump (mm)	Compressive Strength Strength (N/mm^2)		
			7 Days	28 Days	90 Days
100% PC M1	0.35	170	53.7	72.40	84.85
	0.40	131	46.21	69.30	78.35
	0.45	210	39.40	54.35	63.25
70% PC 30% FA M2	0.35	84	28.74	52.09	67.70
	0.45	185	26.50	40.77	49.24
	0.55	98	19.79	26.71	39.29
30% PC 70% GGBS M3	0.40	60	27.36	49.63	70.45
	0.50	140	28.37	50.41	66.15
	0.55	160	13.90	27.92	40.3
85% PC 15% Limestone M4	0.35	120	64.50	81.40	89.45
	0.40	60	57.30	66.35	79.95
	0.45	80	41.91	55.35	59.05

Chloride ingress was investigated by using two different types of rapid chloride migration tests namely Potential Difference test developed at Concrete Technology Unit (CTU) in the University of Dundee (Dhir *et al.*, 1990) and Multi-regime test developed in Spain by Castellote *et al.* (2001).

2.1 Potential Difference (Pd) Test Method

PD test was conducted on 25 mm thick specimens cured for 7 days prior to test. Each specimen was sealed under a diffusion cell containing 800 ml. of deionised water. The cell was then put into immersion tank containing 5-Molar NaCl solution. A graphite rod inserted into diffusion cell and a steel sheet at the bottom of immersion tank was connected to power source, maintaining a potential difference of 7.5V. Chloride concentration was determined by computerised titration method by using nitric acid and silver nitrate. Only 0.5 ml of sample from diffusion cell at 12 hours interval was required for titration. The test runs for 7-14 days. PD index (I) was calculated from the modified Fick's First Law of diffusion as proposed by Dhir *et al.* (1990) which is

$$\ln (C_1 - C_2) = - (IA/V\ell)(t_n - t_o) + \ln C_1 \qquad \text{[Eq 2.1]}$$

Where, C_1 = chloride concentration in immersion tank, ppm; C_2 = chloride concentration in cell reservoir, ppm; I = PD Index, cm^2/s; A = transmission area of the concrete test specimen, cm^2; V = volume of the cell reservoir (litre); ℓ = thickness of test specimen, mm; t_0 = time corresponding to the projection of the abscissa at $C_2 = 0$; t_n = time at conclusion of experiment with concentration in cell of (C_2)

2.2 Multi-Regime (Mr) Test Method

Multi-regime chloride test was carried out as described and developed by Castellote *et al.* [11]. This test consists of two compartments containing 1M chloride solution and deionised water in upstream and downstream cells respectively. When an external potential of 12V was applied, the cathode placed in chloride solution drives the chloride ions to the downstream cell through the specimen where the anode is placed. Determination of the amount chloride concentration is based on measuring the conductivity of the anolyte solution of the downstream cell instead of analysing it. Steady-state (linear relationship between Chloride concentration and time) diffusion coefficient, D_s is calculated from the Modified Nernst-Planck equation, whereas non-steady state diffusion coefficient can also be calculated by considering the time taken by chloride ions to achieve a constant flux. Steady state diffusion coefficient, D_s was calculated from the Modified Nernst-Planck equation

$$D_s = \frac{JRTl}{zFC_1\gamma\Delta\phi}$$ [Eq 2.2]

where, $$J = \frac{(mmol_{ssf} - mmol_{ssi}) \times 10^{-3}}{St_{ss(f-i)}}$$ [Eq 2.3]

Here, J = Flux of chlorides during steady state period, mol/cm^{2}s; S = effective surface area of the test specimen, cm^2; t = duration of steady state, sec; C_1 = Cl concentration in the catholyte , mol/cm^3; γ = activity coefficient of catholyte solution; $\Delta\Phi$ = average effective voltage across specimen, volts ;l = specimen thickness, cm; R = perfect gas constant, cal/mol K ;T = average temperature, °K; z = ion valence, for chloride ; F = Faraday's constant, cal/V

2.3 Difference between Pd and Mr Test Method

Usually results obtained from PD test by using Fick's First Law of diffusion were different than diffusion coefficient resulted from MR tests using Nernst Planck equation. These differences in the results were not only due to use of different equation but also due to the difference in physical and methodological characteristics of these test methods. Differences in salient features of these tests are presented in Table 2.3.

Table 2.3 Comparative features of PD and MR test

	PD Test	Multi-Regime Test
Concrete specimen	100mm Ø, 25mm thick	75mm Ø, 25mm thick
Potential	7.5V dc	12V dc
Orientation	Vertical	Horizontal
Catholyte Type	5 Molar NaCl, in tank	1 Molar NaCl, in cell
Anolyte volume & type	800ml, Distilled water	500ml, Distilled water
Anode type	38mm Ø carbon (inert)	6mm Ø deformed steel bar (corroding)
Cathode type	Stainless steel sheet	6mm Ø deformed steel bar (corroding)
Cathode type	Stainless steel sheet	6mm Ø deformed steel bar (corroding)
By-product	FeCl	Chlorine gas
Measurement	Chloride content titration	Conductivity
Anode-cathode distance	125mm	230mm
Equation	Modified solution to Fick's First law	Modified Nernst-Planck

3. RESULTS AND DISCUSSION

Although concrete mix that satisfies strength requirements may not always be durable against environmental exposures. It is generally assumed that high strength concrete is better in durability. Basis of this assumption may be drawn from the fact that microstructure of concrete influences both its strength and durability. Therefore, a relationship between strength and durability of concrete can be expected. Initially, concrete with 100% Portland cement showed better strength in compressive test than that of concrete with fly ash and GGBS. However, these supplementary materials gained improved strength at later stage. This was due to secondary pozzolanic hydration. This paper focuses its Discussion Mainly On Chloride Durability Aspect Of Concrete Samples.

3.1 Chloride Migration

Like most of the two-cell test methods, the PD and MR tests also use traditional two-cell arrangement, where one compartment contains chloride solution and the other filled with distilled water. Although the basic principle of these tests is same, their geometrical arrangement, analysis method etc are different which result in difference in their measured diffusion indices. Results of rapid chloride migration tests are compared across the effect of w/c ratio, cement types, strength on chloride diffusion. The PD and MR test were conducted on 28 and 90 days old specimen. PD index and Diffusion index were calculated from theE2.1quation ,2.2 and 2.3 .

3.2 Effect of W/C Ratio on Chloride Diffusion

It is a well known fact that chloride diffusion decreases with the reduction in water to cement ratio due to improved pore structure [17]. Effects of w/c ratio on chloride diffusion (PD index) with different cements are shown in Figure 3.1 and 3.2. For all of the mixes it is evident that chloride diffusion rate changes with the change in w/c ratio.

For Portland cement concrete (M1), the changes in PD index for 28 days old concrete with w/c=0.45 was more than 2.5 times greater than the PD index with w/c=0.35 (Figure 3.1). At 90 days, the increases in PD index across these two w/c ratios were roughly similar. Significant changes with varying w/c ratio were also evident in case of Portland-Fly ash (M2) and Blastfurnace (M3) concrete. For both of the cement types, the PD index varied nearly 1.5 times between two immediate w/c ratios at all ages. A different trend was noticed in the case of Portland-limestone (M4) concrete. Although, increase in PD index with increasing w/c was evident, the increase was not as substantial as that of other concrete types. On average, order of 1.2 times increments was evident for two consecutive w/c values at all ages.

A similar tendency of diffusion coefficient with altering w/c ratio was noticed when the specimens were tested by Multi-regime method. Figure 3.3 and 3.4 shows the *D* values at varying w/c ratio for 28 and 90 days old specimens. The diffusion coefficients were distinctly rising with the w/c values.

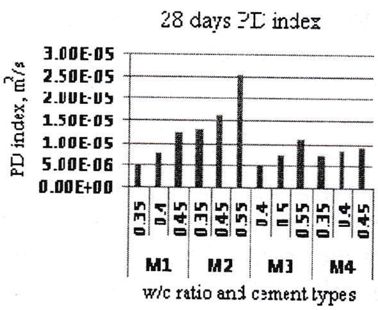

Figure 3.1 PD indices of 28 days old

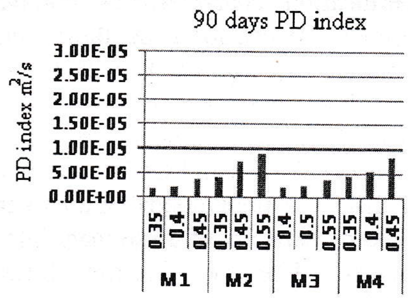

Figure 3.2 PD indices of 90 days old samples

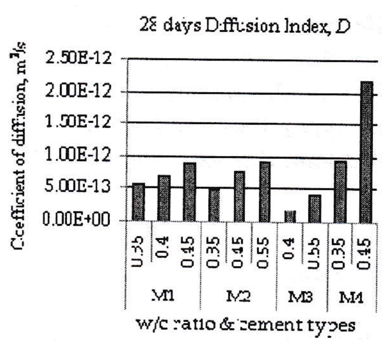

Figure 3.3 Diffusion indices of 28 days old samples

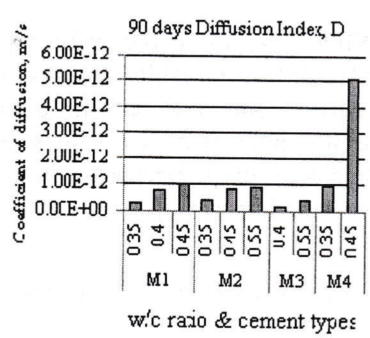

Figure 3.4 Diffusion indices of 90 days old samples

3.3 Effect of Cement Types on Chloride Diffusion

Other than w/c ratio, age and concrete grade of different cement types showed different trend of chloride diffusion when tested with rapid migration tests. It has been reported by several researchers [15, 18-21] that fly ash, GGBS and limestone filler have a beneficial role on the chloride resistivity of concrete. The improvement in chloride resistance is related to a number of physical and chemical characteristics of these cements which result in changes in both microstructure and pore chemistry.

Concrete incorporating fine pozzolanic materials such as fly ash and GGBS offers an enhanced microstructure leading to enhanced permeation characteristics compared to conventional concrete. The higher densification of these materials acts as physical barriers to chloride ion ingress. However, the Portland cement used in this study had finer particles than those of pozzolanic cements. Besides, pozzolanic reaction occurs comparatively in slow pace. Therefore, the beneficial effect of fly ash and GGBS was evident in the later stages than earlier. In addition to their contribution to improved microstructure, the chloride binding capacity of these materials offers the chemical barrier to chloride ingress. Use of ultra-fine limestone filler showed a competitive performance at the earlier ages. However, the performance of Portland limestone concrete against chloride penetration did not change substantially with time.

While examining the influence of different cement types on chloride diffusion, the results are normalised to equal strength, w/c ratio and cement content to see the distinct effect of the materials. Due to the limited number of w/c values (3 for each type), the normalisation of test results required extrapolation to a small extent, this was deemed to be in the safe data range.

3.3.1 Normalised To Equal Strength (55 N/Mm^2)

Figures 3.5 and 3.6 show the PD and MR test results for all cement types normalised to equal strength of 55 N/mm^2. In both cases, GGBS had the best performance among other cement types against chloride intrusion. PD index for M1 concrete is 2.8 times and D value is 5.2 time higher than those of M3 concrete. M1, M2 and M3 showed almost similar trend in both PD and MR test. However, results with M4 are inconclusive.

3.3.2 Normalised to Equal W/C Ratio (0.45)

When the PD test results were normalised to 0.45 w/c ratio, the outcome was slightly different from the strength-normalised data. The difference was significant in case of fly ash combination (Figure 3.7). M3 concrete, this time too, had the lowest PD index at all ages. Fly ash concrete did not show satisfactory result in comparison to M1 concrete at these stages. This may be due to higher specific surface area of M1 cement particles which gave rise to improved microstructure in the early ages. Replacement with limestone filler did not improve the performance at later stages.

3.3.3 Normalised To Equal Cement Content (360 Kg/M³)

From the constituent proportions provided in Table 2.2 it is obvious that the same w/c ratio across different concrete types has the same total cement content. Therefore, chloride diffusion index normalised to equal cement content of 360 Kg/m³ should have similar values as those normalised to equal w/c ratio of 0.45.

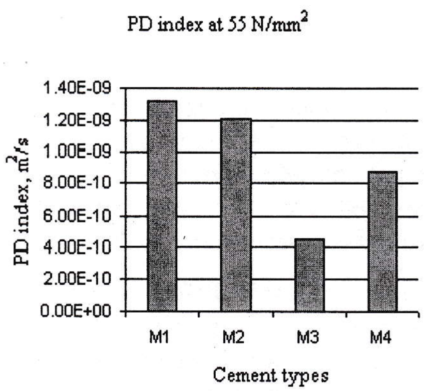

Figure 3.5 PD index at equal strength (55 N/mm²)

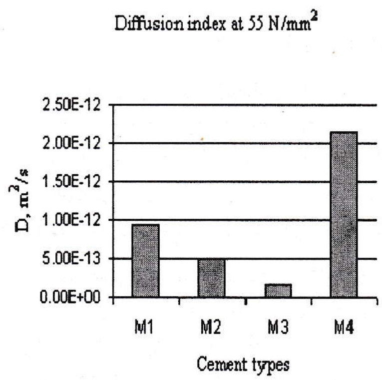

Figure 3.6 Diffusion index at equal strength (55 N/mm²)

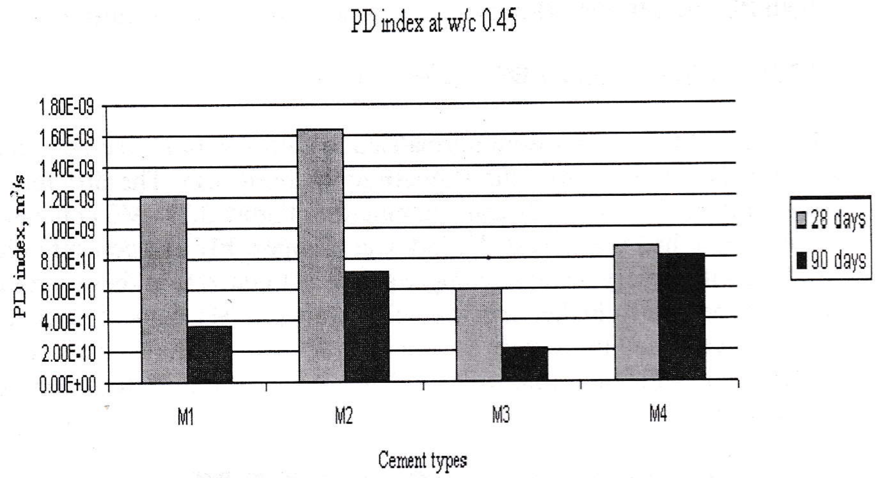

Figure 3.7 PD index at equal w/c ratio (0.45)

3.3.4 Performance at Equal Age

Except M4 concrete other types showed significant decrease in the degree of chloride diffusivity. At 28 days, fly ash concrete demonstrated the weakest resistance against chloride ingress. But at 90 days, the pozzolanic reaction of fly ash and GGBS resulted in better concrete compared to M1 and M4 concrete.

4. CONCLUSIONS

Electro-chemical migration of chloride ions through concrete is influenced by a number of factors. In order to examine the different influential factors, investigations on rapid chloride migration of concrete specimen with different cement types and w/c ratio was undertaken. Following conclusion can be drawn from the experimental results.

Two-cell tests are sensitive to w/c ratio i.e. chloride diffusivity changes with the change in w/c ratio of the concrete specimen. This effect was obvious for all cement types and at all ages. It was evident that higher chloride permeability of concrete was the consequence of increased w/c ratio which in turn was related to the microstructure of the concrete system.

An appropriate mix specification with the limitation on maximum w/c ratio can improve the aspect of durability against chloride penetration. A 2.5 folds decrease in PD index was recorded when the w/c ratio reduced from 0.45 to 0.35 for M1 concrete at 28 days.

In the early ages, M1 concrete performed well against chloride diffusion. Inclusion of limestone did not result in significant benefit. However, with time, fly ash and GGBS concrete showed higher resistance against chloride migration. The competitive behaviour of these pozzolanic cements was significant at later stages of hydration.

At equal strength grade, w/c ratio, cement content and age, GGBS concrete had the highest resistance against chloride among other cement types. The performance was more significant at the later stages.

PD test and MR tests are significantly different from methodological point of view. Conductivity based chloride measurement made MR test less laborious than PD test, which involved additional potentiometric titration to measure chloride concentration. However, the steady state condition was obtained faster in the PD test.

Trend of change in chloride diffusion with w/c ratio, cement types was similar in both tests but the values were different with an order of 10^{-3} ~ 10^{-4}.

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