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ANALISIS OF CORROSION RELATED DURABILITY PROPERTIES FOR REINFORCED CONCRETE CONTAINING LIME STONE POWDER

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ABSTRACT
The lineal range of water-to-cement (w/c) ratios to be used for general construction works is 0.38 to 0.55, considering 'mild' to 'extreme' environments as per IS:456 specifications. Irregardless using such w/c ranges, certain factors such as poor quality materials, improper aggregate gradation, inadequate compaction and curing periods, poor workmanship and quality control practices, etc., can yield poor quality concretes or concretes that are permeable. In addition, specific applications involve concrete to be used for underwater construction, lean construction and others. Although conventional or lower w/c ratios are used in underwater construction, the placed concrete under water may have very high w/c as against the originally designed concrete. In the current study, efforts are taken to study the behavior of high w/c concrete containing limestone powder. While provisions are available to use limestone powder as a partial replacement material for cement as per ASTM, the same is experimented at dosages of 10%, 20% and 40% by mass of cement. The objective of the study is to investigate the ability of limestone powder to serve as a pore filling material for concretes having high w/c ratio.
Eight tests were conducted and attempts were taken to inter relate pore properties of these concretes to their corrosion mitigating ability in microcell and macro-cell corrosion tests using cylinder and prism specimens, respectively. While limestone powder addition was observed to be beneficial at 10% and 20% dosage levels, their addition beyond 20% provided poorer properties in most tests.
KEY WORDS:-Cement Steel, Lime Powder, ASTM, W/C Ratio, Micro-cell Corrosion etc.

INTRODUCTION:

The corrosion of steel reinforcement is one of the greatest concerns in the deterioration of the infrastructure around the world. This chapter will discuss the general mechanism of corrosion, causes of corrosion in concrete and its impact and effect on the structure and in their running life. Finally, the loss of cross section of the reinforcement and its bearing capacity will negatively affect the load bearing capacity and subsequently failure of the structure.
The whole corrosion process is divided into two periods [1],
1. The initiation period
2. The propagation period

In the initiation period, carbonation and chloride ingress take place in the concrete and reaches the steel surface while the propagation period starts when the steel is fully de-passivated and reaches a limiting state when corrosion is unacceptable.

Mechanism of Corrosion

Concrete is a homogeneous material and because of the variation in moisture content, alkalinity within the concrete and bond between the concrete and reinforcing steel bar which causes steel to divide into several cathodic and anodic areas, corrosion takes place. Corrosion comprises of two half reactions, oxidation and reduction that exist and occurs simultaneously at the same rate to ensure evenhanded generation and depletion of electrons for the electro-chemical reaction to continue without any external source to maintain the charge balance [2].

The respective anodic reaction and cathodic is represented by the below mentioned half-cell reactions Eq. 1.1 and Eq. 1.2 while the overall process in concrete Corrosion in Fig 1.1(a) and Different corrosion phases and their volume with respect to "Fe" in Fig 1.1(b).

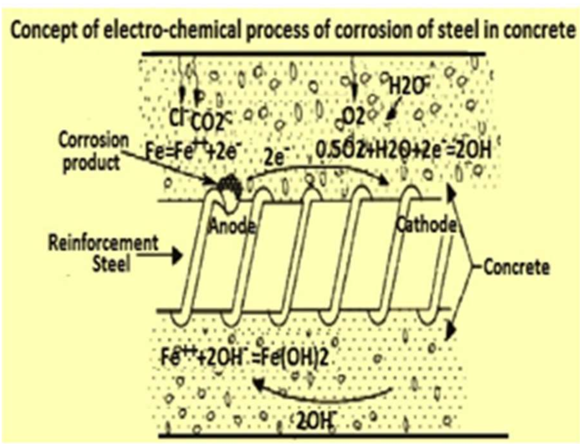


Fig1.1 (a) Schematic diagram of corrosion process in concrete

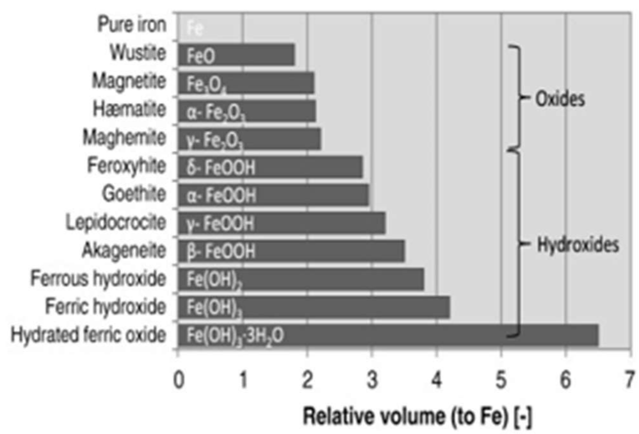


Fig1.1 (b) Different corrosion phases and their volume with respect to Fe

$Fe \rightarrow Fe^{2+} + 2e^-$ Eq. 1.1

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ Eq. 1.2

So, the net or overall reaction comes out to be,

$Fe + O_2 + H_2O \rightarrow Fe^{2+} + 2OH^-$ Eq. 1.3

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$ Eq. 1.4

The combination of Eq. 2.1 and Eq. 2.2 results in Eq. 2.3 and Eq. 2.4, where Ferrous ions (Fe^{2+})ions reacts with hydroxide ion (OH^-) to produce ferrous hydroxide (Fe(OH)2), which forms onthe reinforced steel surface.

The whole process of rust production at steel-concrete surface is shown in Fig 1.2(a) & Fig 1.1(b).

$Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$ Eq. 1.5

$4Fe(OH)_3 \rightarrow Fe_2O_3.H_2O + 2H_2O$ Eq. 1.6

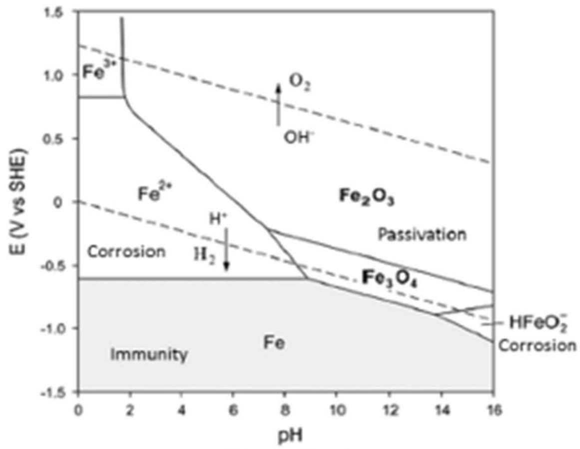


Fig 1.2 (a)

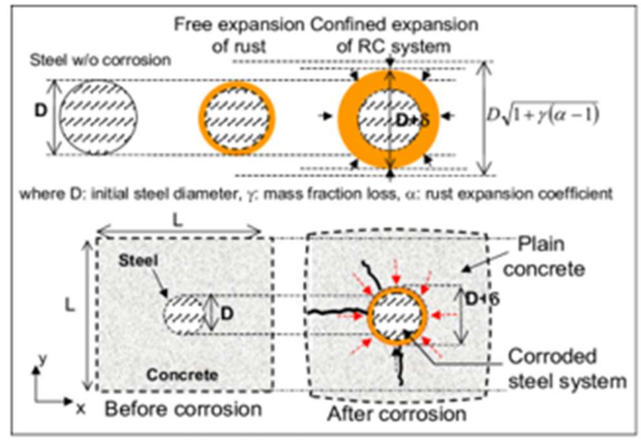


Fig 1.2 (b)

The formation of cracks and then the further spalling is also because of the formation of these corrosion products that are 2 to 7 times of the initial pure iron. The Fig 1.2a and Fig 1.2b shows the variation of corrosion products in terms of volume of the initial pure iron before corrosion.

Types of corrosion

The presence of oxygen and moisture availability, and the resistance offered by concrete are major factors for the phenomenon of corrosion in RC structures. The following are the types of corrosion those can occur depending on the availability of above mentioned factors.

Uniform corrosion: Such type of corrosion occurs uniformly throughout the surface of metal. Generally carbonation causes uniform corrosion

Galvanic corrosion: This type of corrosion occurs when two or more metals having different reduction potentials come in contact with an electrolyte.

Pitting corrosion: This destructive form of corrosion occurs because of the localized break down of the passivity of iron at different locations of the steel reinforcement. Due to small size of the pit, it is difficult to detect. Such type of corrosion is generally caused by chloride attack.

Concentration cell corrosion: In this, the concentrations of soluble ions in the concrete are in such amount that they create a potential difference around the regions of steel bar causing corrosion.

Need for Research

The quality of concrete is dependent on many parameters including w/c, quality of materials, compaction, curing mechanism, workmanship, etc. For most of the above, conventional w/c ratio between 0.40 and 0.55 is usually considered for such application as per IS 456 specifications. In many circumstances, such as (a) concrete placed under water, (b) marine environment, (c) lean concrete and (d) situations where quality control cannot be maintained, studies with high w/c ratio will be helpful. But high w/c ratio in concrete increases its permeability and hence use of such concrete for reinforced concrete structures may not help in protecting steel from corrosion. Very few researches have been performed on high w/c ratios with limestone powder additions.

Objectives of research

The principles objectives of the study are as follows:

1. To determine the effect of limestone powder dosages on the fresh and hardened properties of concrete.
2. To determine the influence of limestone powder addition on the pore structure and conductivity of concrete and its behavior in standard test.
3. To study the performance of highly permeable concretes with limestone powder addition on the micro-cell and macro-cell corrosion using two different specimens.

Previous studies with limestone powder

In the past, various researchers have performed studies with limestone powder as partial cement replacement material in concrete or have directly studied the result of Portland limestone cement with the conventional cement concrete. With the addition of limestone, there is a lot of disagreement regarding the variation in concrete durability properties. Some of which is pointed below. Courard and Michel 2014, Ramezanianpour et al. 2009 and Tsivilis et al. 2002 reported that with use of Portland limestone cement, the workability increases with the increase in the dosage level of limestone [01][02][03]. While Matthews 1994, Fatma et al. 2018 showed decreasing nature of workability with the increase in limestone content. [03][04] For the compressive strength, researches have been performed showing the increase [06] and decrease[36] while mostly showed an optimum limestone content for which there is maximum strength and then gets a decrease [04][07][08][09]. The improvement in strength in initial stages is because of the acceleration effect arises due to filler action of limestone powder relating to the formation of calcium carbo-aluminates hydrates, which increases the rate of hydration. While, in Portland limestone cements, the heterogeneous nucleation and filler effect reacts opposite to the dilution effects which is the reason for having optimum limestone dosages [10]. The decrease in compressive strength is due to decrease in cement content and increase in w/c ratio with the replacement [01]
Experimental Materials

Ordinary pozzolana cement

Ordinary pozzolana cement (OPC) acquired from Ultratech Cement Limited conforming to the IS: 8112 (2013) was used. The chemical and physical properties Bogue's compound composition of the cement are listed in Table .1(a) and Table. 1(b) respectively.

Chemical characteristics	Percentage mass of content in sample (%)	
	Material contains	Allowed as per IS:8112
Magnesia (MgO) content (max.)	2.65	6.00
Loss on ignition (max.)	4.80	5.00
Total sulphur content (max.)	2.35	3.50
Chloride (Cl) content (max.)	0.011	0.100
Declared % of Fly ash in OPC	0.00	5.00

Table .1(a) The chemical composition of the cement

Physical characteristics	Content in sample	
	Material contains	Allowed as per IS:8112
Fineness, m^2/kg	276	225
Soundness: IS 4031 (Part 3)		
a) By Le Chatelier method, mm (max.)	9.50	10.0
b) By autoclave test method, percent (max.)	0.800	0.800
Setting time		
a) Initial, min, (min.)	240	30.0
b) Final, min, (max.)	420	600
Compressive strength		
a) 3 day MPa (min.)	23.0	23.0
b) 7 day MPa (min.)	33.0	33.0
c) 28 day MPa (min.)	43.0	43.0

Table .1(b) The physical properties of the cement

Sand

The fine aggregates used is river sand, conforming to IS: 383 specifications following the gradation zone III.

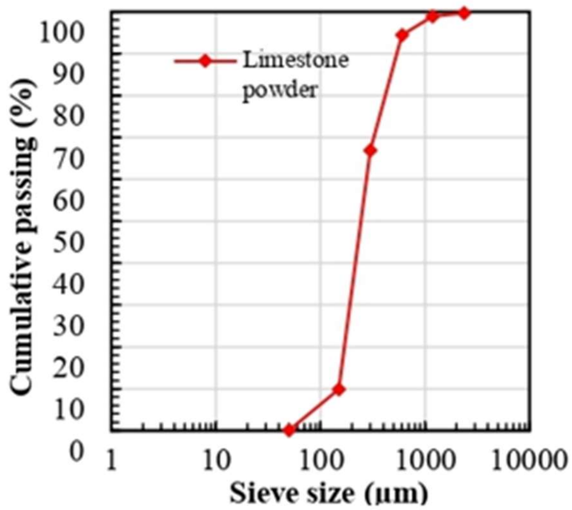
Limestone powder

The fine powder used in the study as a cement replacement is limestone powder. Various chemical compositions are listed in the Table .1(c)

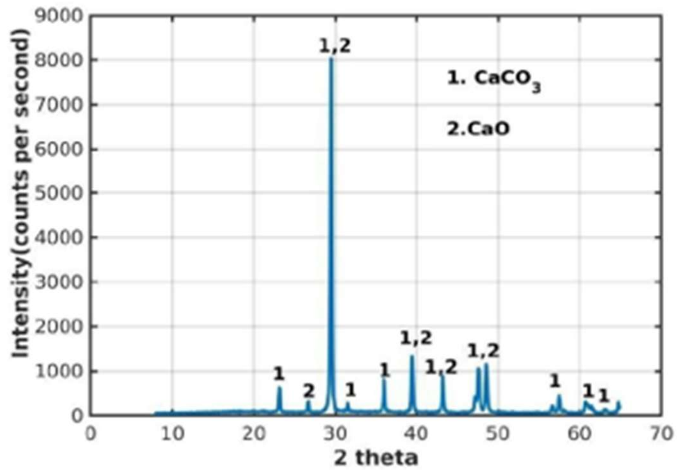
Material	Oxide composition (% by total mass)							
	CaO	Fe_2O_3	Al_2O_3	SiO_2	MgO	MnO	P_2O_5	TiO_2
Limestone powder	78.9	2.80	0.86	16.3	0.65	0.07	0.14	0.14

Table .1(c) The chemical composition of the Lime Stone Powder

The gradation and the X-ray diffractogram is shown in the Figure 1.4 and Figure 1.5



• **Figure 1.4**



(c) X-ray diffractogram analysis for the Limestone powder

Figure 1.5

Coarse Aggregate

The coarse aggregates used are in the range of 4.75 mm to 19 mm with a sieve no.7 as per ASTM C33 code specifications.

Reinforcement

The reinforcement used is Fe500 SAIL TMT bars of 12mm diameter with the average yield strength of 525MPa (taken average of 3 samples). The steel properties are conformed with the IS: 1786 standard.

4.2 Mixture Proportioning

The mixture proportion is taken to be 1:1.5:3 of cement, fine aggregates and coarse aggregates respectively. The dosage of limestone powder is taken to be 0%, 10%, 20% & 40%. The finalized mixture proportions are shown in Table 4.7.

Table .1 (d) Mixture proportion of Concrete specimens

Mixture IDs	w/cm	Quantity of materials (in kg per m³ of concrete)				
		Cement	Sand	Coarse aggregates	Water	Limestone
LP-0%	0.6	363	545	1091	218	0
LP-10%	0.6	326	544	1089	217	36
LP-20%	0.6	290	544	1087	217	72
LP-40%	0.6	216	541	1083	217	144

The different mixture IDs and their description are shown in Table.1 (e).

Table1. (e) Mixture IDs and description

Mixture ID	Description of mixtures
LP-0%	Control mixture with 0% powder addition at 0.60% w/cm ratio
LP-10%	Control mixture with 10% limestone powder addition at 0.60% w/cm ratio
LP-20%	Control mixture with 20% limestone powder addition at 0.60% w/cm ratio
LP-40%	Control mixture with 40% limestone powder addition at 0.60% w/cm ratio

EXPERIMENTAL PROGRAM

This contains brief explanation of procedures of several tests used in the study which formulate the durability and mechanical strength of the concrete made with internal carbon viz., compressive strength test, electrical resistivity, rapid chloride ion, permeability test, water absorption, sorptivity test, half-cell potential test, macro-cell current measurement, gravimetric method and fourier transform infrared spectroscopy.

Test methods for determining the mechanical and durability properties of concrete containing limestone powder

Table 5.1 Details of standard test methods used in Part I of the program

Tests*	Test Method	Salient features
Compressive Strength	IS:516	* Load rate = 35 N/mm^2/min as per IS 4031 (Part VI). * Specimens: Cubes of size 150 mm as per IS: 516.
Rapid Chloride Permeability Test	ASTM C1202	* Specimen: Cylinder of height 50 mm & diameter 100 mm. * Conditioning as per ASTM C1202. * Placed between 3% NaCl solution (-) and 0.3N NaOH solution (+). * Potential of 60V is applied for 6 hours and Current is monitored.
Surface Resistivity Test	ASTM C1760	* Specimen: Cylinder of height 200 mm & diameter 100mm. * Readings were obtaining by using instrument (Resipodproceq). * Exterior electrodes pass electric current though concreteand interior electrode measure the resultant voltage. * Average of 8 values along the surface is taken.
Water Absorption Test	ASTM C642	* Specimen: Cylinder of height 50 mm & diameter 100 mm. * Specimen kept in oven, immersed in water, boiled at 100□C for fixed period of time. * Weight of specimen after each action is measured.
Sorptivity Test	ASTM C1585	* Specimen: Cylinder of height 50 mm & diameter 100 mm. * Conditioning performed as per stated in ASTM C1585. * Epoxy coated at curved surface & tape wrapping at top surface. * Water poured up to 5cm in the acrylic mould. * Weight of specimen was measured after 1, 5, 10, 20, 30, 60 minute,

		after which the recordings were taken every 1 hour until 6 hours and every day until 7 days.

Test-Set-up 1 (on cylindrical specimen)

Half-Cell Potential Test as per Standard Test Method for Half-Cell Potentials of Uncoated Reinforcing Steel in Concrete (ASTM C876)

In this method, the potential difference between the bars and the standard reference electrode is measured by applying electric current and the data is used to predict the extent of corrosion in the specimen using ASTM C876. Concrete cylinder specimens (having a steel bar embedded centrally inside) were dipped in a bath containing NaCl solution up to a depth of 150 mm and Cu/CuSO4 standard reference electrode were placed over the concrete.

Gravimetric method

In gravimetric method, the corroded bars after performing the test mentioned in previous section was completely removed from the main specimen and immersed in properly prepared Clarke's solution [i.e., 1000 ml HCl with specific gravity of 1.19 + 20g of antimony trioxide (Sb2O3) + 50g of stannous chloride (SnCl2)] as per the ASTM G1-90 specifications to effectively remove the corrosion products at lab.

Accelerated corrosion test

In this test, the corrosion process is accelerated by using impressed voltage technique and has been used by many other researchers. Here, the steel bar in concrete is corroded in relatively shorter time by applying a current through a voltage of 3V in which the stainless steel plate acts as a cathode (negative terminal) and steel bar acts as an anode (positive terminal).

Fourier Transform Infrared (FT-IR) Spectroscopy

In this study, FT-IR measures the absorption of infrared radiation by the sample material vs wavelength to observe properties of the rust sample. When a material is exposed with infrared (IR) radiation, the IR absorption bands identify the molecular components and structures present in the sample. The absorbed IR radiation excites molecule into a higher vibrational state and based on the characteristics of the molecule, the wavelength of light is absorbed which in turn is a function of the energy difference between the vibrational states at rest and in excited condition.

EXPERIMENTAL PROCEDURE

This chapter includes program and experiment matrix of different test performed, to fulfill the objectives of this work. The Part A includes the design of various mixtures, their casting and curing. The type of the specimen used for this study is of two kinds. The first being the cylindrical specimen of 100mm dia. and 200mm ht. as shown in Figure 2.1. The cover here is maintained around 44mm. The second being the prism specimen of size 280mm x152mm x 115mm as shown in Figure 2.2. The design is done with the variables being the percentage replacement of cement with limestone at levels of 0%, 10%, 20% and 40%.

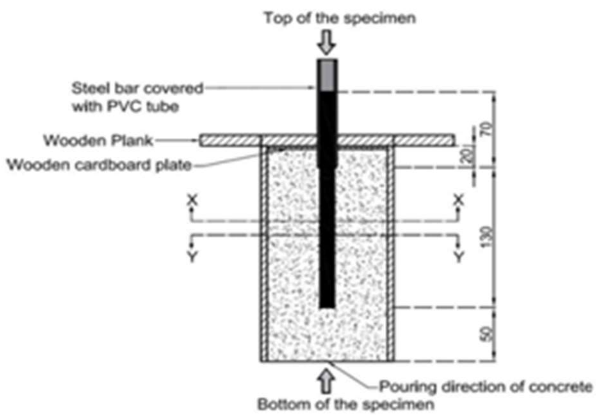


Fig 2.1 cylindrical specimen

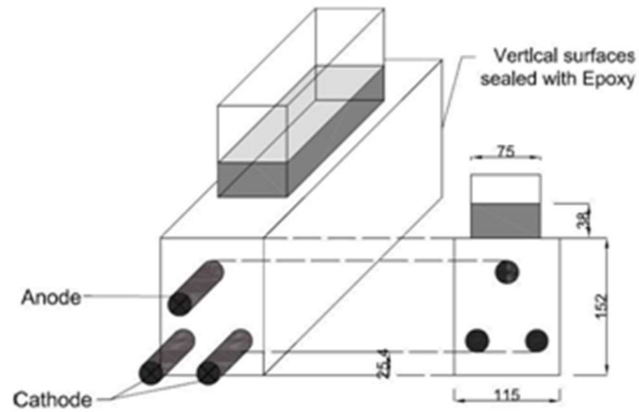
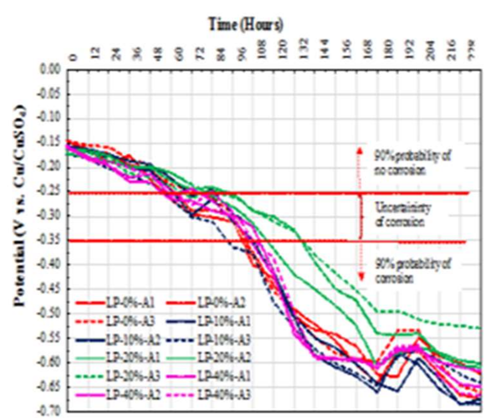
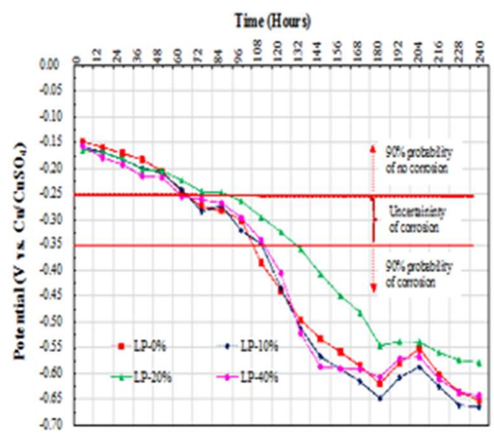


Fig 2.2 prism specimen

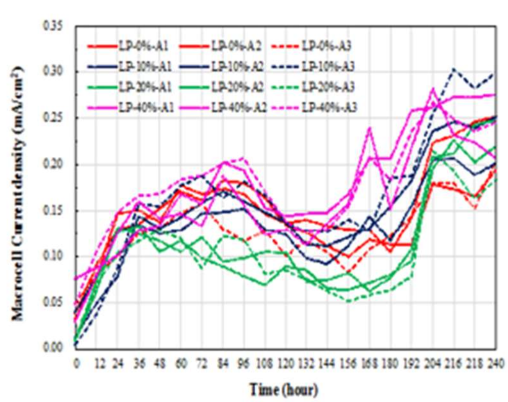
The Second part, i.e. Part B includes the electrochemical setup of the concrete-reinforcement specimen viz. cylindrical and prism specimen for the corrosion studies/tests. This includes the accelerated corrosion setup and various corrosion tests such as half-cell potential and macro- cell current test (only for ASTM G109 Prism specimen) that works on the principle of disturbing the equilibrium through external force, here it is voltage and current and measure the response in the form of current and voltage.



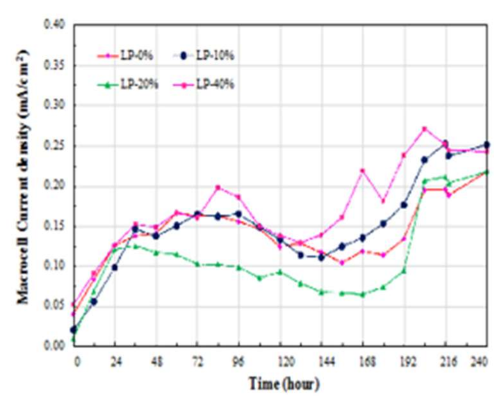
(a) Half-cell potential values of the steel bar with all prism specimen



(b) Half-cell potential values of the steel bar with average of 3 prism specimen

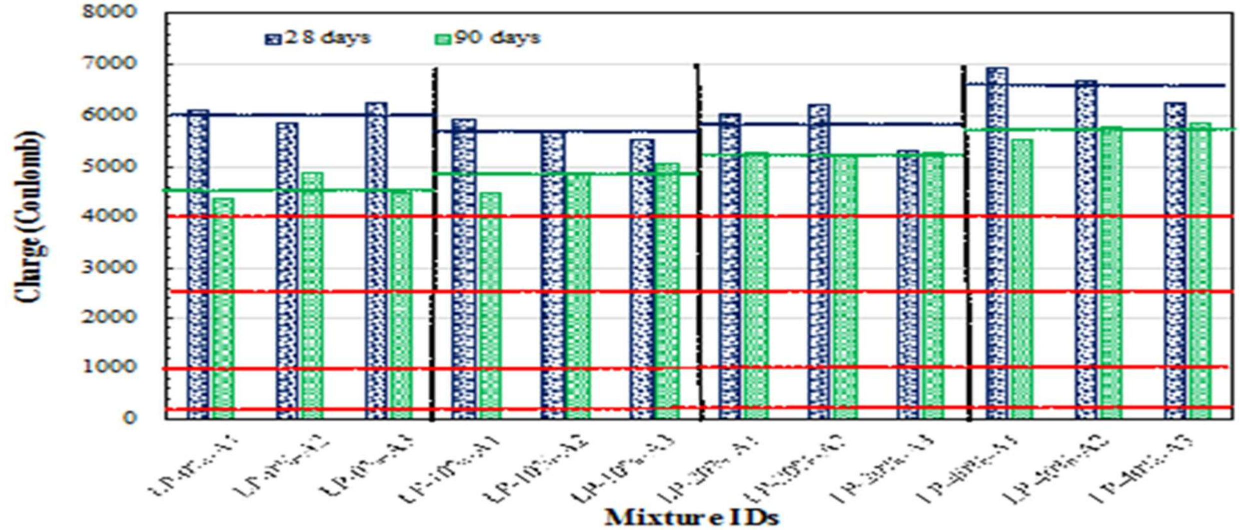


(a). Plot of Macrocell current vs Time of all ASTM G 109 prism specimen



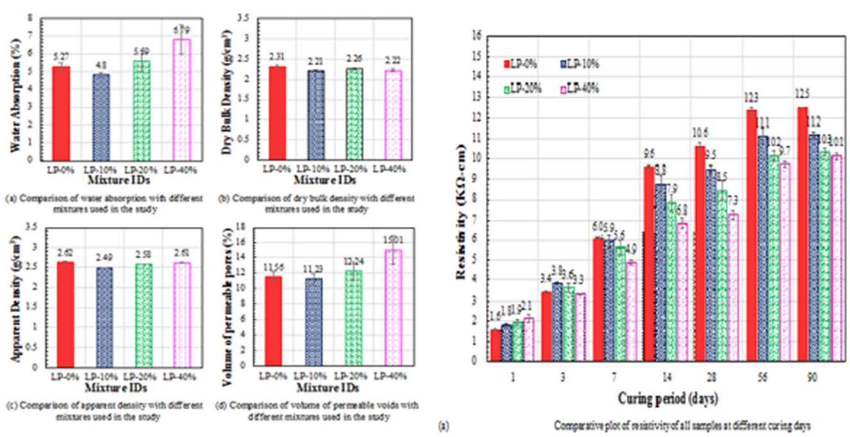
(b). Plot of Macrocell current vs Time of average 3-ASTM G109 prism specimen

Part C includes the various fresh, mechanical and durability property testing of concrete with limestone powder. The strength properties include compressive strength of hardened concrete cured for 1, 3, 7, 28 and 90 days while the durability properties include rapid chloride penetration test and resistivity measurements.



(a) Comparative plot of rapid chloride ion permeability of all mixtures used in this study

The final part, i.e., Part D that includes the pores property determination through water absorption test, sorptivity test, resistivity and rapid chloride ion permeability test to conclude the pore nature and volume of permeable pores of the test mixtures with limestone as cement replacement.



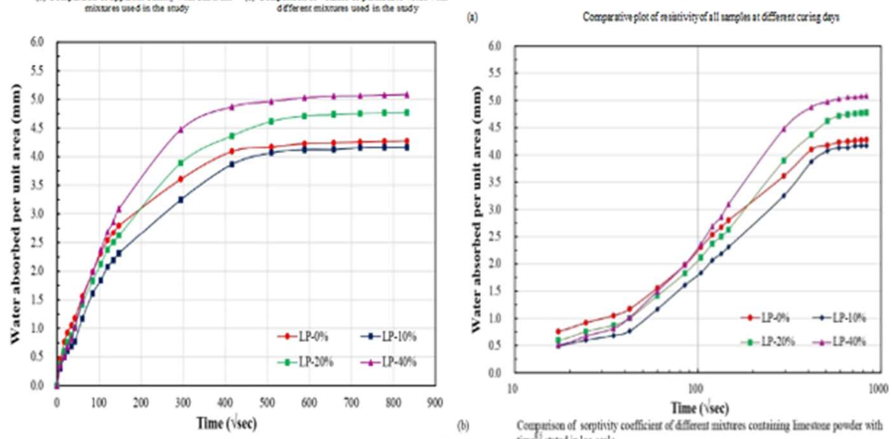
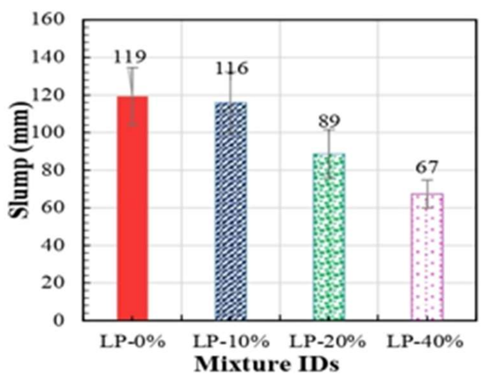


Figure 6.4 Sorptivity test results

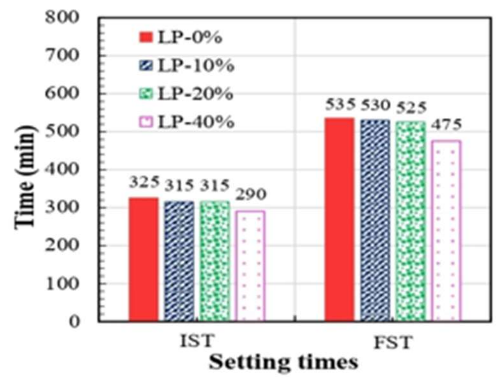
Effect of Lime Stone Powder on fresh properties of concrete

(i) Shear slump (ii) Collapse (iii) True slump (iv) True slump

(a) Photograph showing the effect of limestone powder on the slump of concrete



(b) Comparison of workability test results of mixtures containing limestone powder



(c) Comparison of IST & FST results of mixtures containing limestone powder

CONCLUSION

Effect of Limestone powder on the fresh properties of concrete

The fresh properties of concrete including workability (slump) test, setting times are shown in above Figure in part (a), (b) and (c) respectively. The workability levels of 67 mm to 119 mm achieved in this study is within the prescribed place-able situation provided in section 7.1 of IS 456. Most applications fall under this workability criterion. As the Figure shows, the workability decreases by 0% to 44% with increasing limestone content from 0% to 40% respectively due to dilution effect, arises due to low specific gravity of limestone powder resulted in high surface area, which further increases the water requirement.. Also, the fineness of limestone is found to be not dominant as the other factors that affecting the workability in adverse scenario.

The IST and FST are performed using penetration resistance setup using a defined area of needles to penetrate into the mortar sieved from the different mixtures. As shown in the Figure, mixes with 0%, 10% and 20% limestone powder replacement, no change is seen in initial and final setting time. The IST ranges from 315 to 325 minutes while the FST lies from 525 to 535 minutes. The mixture LP-40% has relatively lower IST and FST than others, taking 30 minutes to get initial penetration resistance of 3.43 MPa while 50 minutes less to get the final penetration resistance of 26.97 MPa. This is because of the reduction in C3A content or reduction in nucleation stage affecting the stage

I, i.e. heat of dissolution and stage II, i.e. induction period later decreasing the total initial and final setting time of the mixtures.

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