STUDIES ON DURABILITY PERFORMANCE OF CONCRETE UNDER MARINE ENVIRONMENT INCORPORATING METALLIC SLAGS AS SAND REPLACEMENT

Thesis

Submitted in partial fulfilment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

by

ARPITHA D

(165107CV16F04)

DEPARTMENT OF CIVIL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY KARNATAKA

SURATHKAL, MANGALORE – 575 025

APRIL 2022

STUDIES ON DURABILITY PERFORMANCE OF CONCRETE UNDER MARINE ENVIRONMENT INCORPORATING METALLIC SLAGS AS SAND REPLACEMENT

Thesis

Submitted in partial fulfilment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

by

ARPITHA D
(165107CV16F04)

Under the guidance of

Dr. C. RAJASEKARAN
Assistant Professor

DEPARTMENT OF CIVIL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY KARNATAKA

SURATHKAL, MANGALORE – 575 025

APRIL 2022

DECLARATION

I hereby *declare* that the Research Thesis entitled "**Studies on Durability Performance of Concrete under Marine Environment Incorporating Metallic Slags as Sand Replacement**", which is being submitted to the **National Institute of Technology Karnataka, Surathkal** in partial fulfilment of the requirements for the award of the Degree of **Doctor of Philosophy** in the **Department Of Civil Engineering** is a *bonafide report of the research work carried out by me*. The material contained in this Research Thesis has not been submitted to any University or Institution for the award of any degree.

Arpitha D

165107CV16F04, ARPITHA, D.
Department of Civil Engineering
National Institute of Technology Karnataka, Surathkal

Place: NITK-Surathkal

Date: 12/04/2022

CERTIFICATE

This is to *certify* that the Research Thesis entitled **STUDIES ON DURABILITY PERFORMANCE OF CONCRETE UNDER MARINE ENVIRONMENT INCORPORATING METALLIC SLAGS AS SAND REPLACEMENT** submitted by **Ms. ARPITHA D.** (Register Number: 165107CV16F04), as the record of the research work carried out by her, is accepted as the Research Thesis submission in partial fulfilment of the requirements for the award of degree of Doctor of Philosophy.

12/04/2022

....

Dr. RAJASEKARAN, C.
Assistant Professor
Department of Civil Engineering
National Institute of Technology Karnataka, Surathkal

DEPT. OF CIVIL ENGG.

....
Chairman – DRPC
Department of Civil Engineering
National Institute of Technology Karnataka, Surathkal

Chairman (DRPC)
Department of Civil Engineering
National Institute of Technology Karnataka, Surathkal
Mangalore - 575 025, Karnataka, INDIA

ACKNOWLEDGEMENT

With a deep sense of gratitude, I express my heartfelt thanks to my research supervisor **Dr. Rajasekaran**, **C.** Assistant Professor, Department of Civil Engineering, NITK Surathkal for his invaluable guidance, encouragement, and motivation throughout my research work. His moral support, interactions, discussions, and precious suggestions have greatly helped me to complete this research work. It has been my greatest opportunity and pleasure to work under him. His crucial comments have guided me to publish my research work in acclaimed International Journals.

I would also like to convey my sincere thanks to my Research Progress Assessment Committee members, **Dr. B. B. Das**., Department of Civil Engineering, NITK SURATHKAL and **Dr. M. R. Ramesh**, Department of Mechanical Engineering, NITK Surathkal for providing valuable suggestions, comments, and encouragement at various stages of this research work.

I would like to thank **Prof. B.R. Jayalekshmi**, Head of the Department of Civil Engineering, NITK Surathkal, and the former Heads of the Civil Engineering Department, for all the support throughout my stay at the NITK Surathkal campus.

I am also thankful to all faculty and non-teaching staff and office staff of the Civil Engineering Department for their help and support.

I owe my special thanks to **Dr. M.C. Narasimhan**, Professor, Department of Civil Engineering, NITK Surathkal for providing insight knowledge for my research work.

My sincere thanks to **Dr. Katta Venkataramana**, Professor, Department of Civil Engineering, NITK Surathkal for his great support and guidance.

My sincere thanks to **Er. Nagesh Puttaswamy**, Zonal Head, Ultra Tech, Bengaluru, for his great support and guidance in every step of my research work.

My special thanks to **Prof. M.S. Shetty**, the author of the Concrete Technology book, for his invaluable guidance and blessings to carry out this research work.

I would like to express my deepest gratitude to **Mr. Manohar Shanbhogue K**, Senior Technical Assistant, Environmental Laboratory, Department of Civil Engineering, NITK Surathkal. for his valuable guidelines. My special thanks to **Mr. Dheeraj**, Lab

Assistant, Environmental Laboratory, Department of Civil Engineering, NITK Surathkal.

My sincere thanks to Mr. Satish, R&D, JSW Bellary, Karnataka, and his team for providing information on the processed granulated slag and the material to carry out the work.

My sincere thanks to Mr. Ranjith, Sterlite Industries, Thootukudi, Tamil Nadu for providing information on the copper slag and the material to carry out the work.

My wholehearted thanks to **Dr. Rana Prathap Reddy**, Principal, Global Academy of Technology, Bengaluru for his support and interest in every phase of research work.

I am filled with profound gratitude to **Dr. Premakumar**, former Professor, REVA University, Bengaluru, for keeping hopes on me and his blessings.

My heartfelt thanks to Dr. Prathap Kumar, Head of the Department, Civil Engineering, R.N.S Institute of Technology, Bengaluru, for his immense motivation and support to carry out this work.

I would like to express my gratitude to Mrs. Leelavathi, former Professor, REVA University, for her motherly support to fulfill my desires throughout my work.

I would like to offer my special thanks to Dr. Ramesh, R.L, Head of the Department, Civil Engineering, Don Bosco Institute of Technology, Bengaluru, for concreting the world of concrete technology in my career.

I am overwhelmed with gratitude to the team of Technical Services Ultra Tech Ltd. Bengaluru, Mangalore, and Udupi for their kind support and guidance.

I owe my best thanks to Dr. Raghavendra Holla, President, J.C.I Mangalore Samrat, Mangalore for providing me his valuable contacts and support.

I was dazzled by the generosity of Mr. Rasheed and team, fishermen Surathkal, without whom it would not have been possible to carry out the practical works in the sea.

I owe a very important debt to my co-workers Mr. Muttu, Mr. Ravi, Mr. Raju who has contributed equally in every step of the research work.

I gratefully acknowledge the emotional support and encouragement provided by my friends Pandith Aradhya B J, Chethan Gowda, Krishnamurthy M P, Venkatesh Patil, Virupaksha, Pramod M, Amulya M and family, Buvanesh. C and family, Suman Saha, Basavana Gowda S N, Sharath. Swarup, B.P, Tilak Y.T, Sudarshan V.J, Niranjan Gachinamath, Vivek Kele, Likitha N, Swathi S, Shubha, Suma, Girish G N, Sunil Meti, Harish Kumar, Vijay Kumar, Harish who have helped me to collect data, write the paper, and thesis and who pushed me every time to walk extra-mile towards the goal.

I am indebted to the support, technical suggestions, and all the help rendered by Dr. Rahul A V, Post Doc student, Ghent University, Europe, whose contributions during paper writing and correction are incredible.

My special thanks to the Kannada Vedike team who stood by me throughout this journey with his support, suggestions, and timely help extended at NITK.

I am in debt thankful for Mrs. Sumathi, Mrs. Vidya, and Mrs. Prathima, coffee shop, Mrs. Bhagya, Security guard, and Mr. Dhananjay Shetty, GH mess in charge at NITK SURATHKAL for providing me a homely atmosphere.

I am forever grateful to my father **Sri. Dhananjaya**, **mother Smt. Sudha Devi S**, my grandfather late Sri.Sri Rangiah and family for playing a crucial role in modeling me My deep gratitude for their kindness, unwavering support, and sacrifices throughout my life for proving the best education and encouragement in all my endeavors.

I am deeply grateful to my uncle Mr. Jayakeerthi S and his friends, for introducing and bringing me up in the field of civil engineering by providing generous support, insightful comments, and suggestions in my profession.

My special thanks and regards to Mr. Sujay S, for being there as my best friend as a guardian and mentor for standing by my dreams and passion, providing constructive comments and warm encouragement in every walk of my life.

I feel blessed and happy to receive them as my dear friends, Mr. Krishnamurthy T, Mr. Agadi Kishan, Mr. Krishnamurthy, Mr. Subramanya, Mr. Rajeev, Mrs. Shylaja, Mr. Ullas team, and colleagues of REVA who have been influential in motivating me in this journey with their moral support and cooperation.

I lovingly acknowledge the moral support and help extended by my research colleagues during this journey. Their informal support and encouragement have been very crucial. I am grateful to everybody who helped and encouraged me during this research work.

Arpitha D

Dedication

With genuine gratitude and warm regard, I dedicate my research
work to my proud motherland

“INDIA”

To all the Civil Engineers and Covid Warriors in the world
for their eternal love and contribution

ABSTRACT

An investigation was carried out to examine the aggressive effects of seawater on concrete specimens. The concrete specimens were prepared by partially replacing fine aggregates (0% to 50%) from copper slag (CS) and processed granulated blast furnace slag (PGBS) and subjected for 7, 28, 56, 90, 180, 270 and 365 days of curing. Compressive and splitting tensile strength tests were conducted at different ages after immersion in both fresh and seawater. Durability tests for chloride attack, sulphate attack, and sodium were conducted using the toxicity characteristic leaching procedure (TCLP) method. Test results revealed that the compressive and splitting tensile strength of CS and PGBS concrete cured in seawater was higher than that of cured in freshwater. Also, the concentration of chloride and sulphate ions of CS and PGBS concrete were lesser when compared to the control mix. Scanning electron microscope (SEM) analysis of specimens showed that the PGBS and CS concrete showed a denser ITZ at latter ages which may be due to the additional C-S-H formed from the hydraulic reaction of the slag aggregates. Present study shows that more durable and sustainable concrete can be designed for marine applications by partial incorporation of suitable low-cost and eco-friendly alternatives in contrast to natural fine aggregate (NFA- river sand).

Keywords: Copper slag, Processed granulated blast furnace slag, Seawater, Chloride attack, Sulphate attack.

.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS

w/c	Water-Cement ratio
NFA	Natural Fine Aggregate
FA	Fly Ash
SF	Silica Fume
CS	Copper Slag
IS	Iron Slag
GBFS	Granulated Blast Furnace Slag
PGBS	Processed Granulated Blast Furnace Slag
OPC	Ordinary Portland Cement
SP	Superplasticizer
PCE	Polycarboxylate ether
LS	Lignosulfonate
SNF	Sulphonated Naphthalene Formaldehyde
FW	Fresh Water
SW	Sea Water
DO	Dissolved Oxygen

CHAPTER 1

INTRODUCTION

1.1 GENERAL

Deterioration of concrete is a recognizable, undesirable state which is not a portion that is originally intending to design concrete structures, presently has to turn out to be an intense topic of significance for researchers. The aggressive impact on concrete for innovative investigations and a few essential pieces of evidence perseveres to be the dynamic focus that has been already cited. Concrete is prone to primary disintegration when subjected to the marine environment, though constantly verified for a superior structural and durability performance.

Apart from traditional port structures, many structures are being constructed these days along the coasts for scientific exploration. The exploitation of ocean depth accelerated attempts to avail natural resources of the ocean. These structures also include accessible transportation facilities like a harbour and off-shore constructions, pipelines, etc. All of these come in constant contact with seawater which is highly corrosive to the performance of the construction materials. Also, a good number of structures are being built along the coastline for hinterland development. These are also subjected to the sea breeze's aggressive action, which carries many chloride ions and moisture. This increase in marine construction activity has posed a challenge to the ingenuity of the designers of structures and builders. The facilities for them must be tailored to meet the hostile ocean environment. Before selecting materials for the construction of such structures, many factors must be taken into account. Among these are the initial cost of materials and their efficiency in the intended design, the predicted lifetime of the materials as influenced by corrosion processes, and interaction of stresses. The performance of behavior of many materials individually or in combination in seawater or marine atmosphere is too complex to predict.

The marine environment is any place where concrete becomes wet with seawater. This could happen to concrete submerged underwater, in the tidal zone, splash zone, or inland where the wind could carry the salt-water spray. The marine environment consists of various active physical, chemical, and biological agents. Seawater contains various aggressive salts such as chlorides, sulphates, combined alkalis with magnesium, etc. Moreover, wave actions, cross currents, and tidal effects are present in the marine environment. The structure subjected to the above environmental conditions consists mainly of concrete and steel. The constituents of concrete and environmental exposure conditions play a vital role in the long-term performance of marine concrete structures (both reinforced and pre-stressed). The marine environment includes the mud zone, submerged zone, intertidal zone, splash zone & atmospheric zone.

1.2 EFFECTS OF SEA WATER ON CONCRETE

Seawater consists of sodium, chloride, calcium, magnesium, and potassium ions as major chemical constituents. The reaction caused initially between potassium and magnesium sulphates present in seawater and calcium hydroxide $Ca(OH)_2$ leads to sulphate attack during the process of hydration of dicalcium silicate (C_2S) and tricalcium silicate (C_3S) existing in cement. The significant reaction between magnesium sulphates and chemicals present with seawater results in the formation of soluble magnesium hydroxide ($Mg(OH)_2$), which damages the concrete outcomes in the formation of gypsum (Swamy and Hung 1998). The penetration of chloride ions into the concrete results in accelerated corrosion of the reinforcement as seawater consists of 35,000 ppm of dissolved salts, and the pH of seawater lies in the ranges of 7.4 to 8.4. Also, the chances of corrosion of reinforcing steel occur below a pH of 11 (McCoy 1966). The alkali-aggregate reaction intensifies due to sodium and potassium ions, thereby weakening the cement paste. This showed that the initial concern is not with the reaction between the high chloride content of seawater and cement paste. (Uddin et al. 2004).

1.3 REVOLUTION IN CONCRETE INDUSTRY

The integration of composites progresses the performance of the hardened properties of concrete, thus offering resistance to marine conditions (Liu et al., 2002). The concrete prepared with seawater may show higher strength at premature ages related to control concrete, and the reduction in strength in the future can be overcome by decreasing the water-cement ratio (w/c) (Shayan et al. 2010). As a replication to this development, today cement, and concrete industries are gradually becoming more attentive regarding advancement towards environmental and other sustainable issues. In this aspect, the application of various researches has been kept in place, and the results emerged in bringing the solution in terms of alternative materials to be used as natural fine aggregate (NFA) in concrete to decrease the problem of the environment that is being expansively examined all over the world and looking to the significance of necessities, properties and quality owing to the global consensus on the materials. The industrial by-products having pozzolanic features may partly replace the materials and identified advantages on the durability of the products like fly ash (FA), silica fume (SF), copper slag (CS), and iron slag (IS), etc., are incorporated with the construction materials. These industrial by-products are bowed into a valued product and lessen environmental contamination. Thus, improve durability, compressive strength, and flexural strength in the concrete.

The effective utilization of CS, steel slag, etc., as an alternative to NFA in cement mortar and concrete, has been beneficial environmentally and economically. Today the construction industry is concentrating on reducing the water-cement ratio and compatibility issues, thereby enhancing the workability, strength properties with the incorporation of superplasticizers in the concrete mixes, which has been underscored in the emerging trend of concrete preparation which imparts desirable properties in both plastic and hardened state. Experimental Investigations have been carried out to improve the rheological and mechanical properties by incorporating various fine particles like granulated blast furnace slag (GBFS) etc., where mineral admixtures have actively contributed to the enhancement of workability in the fresh state and to develop greater strength due to their pozzolanic reaction and latent hydraulic properties The rheology of fresh cement paste is integrated with the evolution of microstructure in cement mortar and concrete. Considering the behaviour of blended cement on the addition of mineral admixtures is crucial as it will have a direct impact on the microstructure of fresh cement paste, which increases yield stress and thereby decrease plastic viscosity (Burgos-Montes et al. 2012). The reduction of both w/c ratio improves strength and workability, the addition of superplasticizers effectively decreases the capillary porosity and permeability. Thus, it helps to reduce the heat of hydration and improve the concreting process in hot climates and marine structures.

1.4 ORGANIZATION OF THESIS

The thesis is presented in six chapters. The content of each chapter enclosed in detail is explained as follows.

Chapter one provides a section of general information about the deterioration of concrete. The observation on the impact of sea water on concrete deals with the type of aggregates required for the proper mix proportion of concrete, and its serviceability is discussed. Also, advanced studies on the availability of materials to increase the durability of concrete are mentioned.

Chapter two delivers a review of the past research works carried out related to the causes and effects of sea water on concrete. The effective studies carried out to overcome the deterioration of concrete are presented. The importance of the selection of the materials used in concrete, its composition, and applications are noted. The need for utilization of the new alternative materials in the concrete, especially as a replacement for the natural fine aggregates has been studied.

Chapter three deals with the properties of the materials used in the present study and the methodology adopted to carry out the research work.

Chapter four discusses the results in detail obtained based on the tests carried out on the concrete specimens.

Chapter five discusses the conclusions and the contribution drawn from the observation made in the present study.

1.5 CLOSURE

To achieve a sustainable environment, sand extraction from the rivers has tried to demand the implementation of recovery and rehabilitation measurements over the affected areas, thus seeking applied environmental safety control studies. About 75%

of the total volume of concrete is constituted by fine and coarse aggregate. Researches on CS is still less even though several advantages are found concerning possibilities of using CS in various fields. Similarly, the utilization rate of processed granulated blast furnace slag (PGBS) is an imperative way for the steel enterprise to realize sustainable development. Therefore, improving the research progress of CS and PGBS utilization in the marine environment is presented in this research work. This study aims to determine the durability effects of the new alternative materials as a partial replacement in concrete to provide a solution for concrete deterioration when exposed to the marine environment.

CHAPTER 2

LITERATURE REVIEW

2.1 GENERAL

Concrete has long been known as reliable construction material, but deficiencies in material selection, detailing, and design can affect the service life of the concrete. Deterioration of concrete structures can become a challenge for the owners of these structures. It is important to identify these defects on time and plan appropriate repair strategies. The most common defects observed in the existing structures are scaling, disintegration, erosion, corrosion of reinforcement, delamination, spalling, alkali-aggregate reaction, cracking of concrete (before hardening due to settlement within concrete mass and plastic shrinkage. In case after hardening, it is due to drying shrinkage, thermal contraction, and sub-grade settlement). Typically, one or a number of these defects can be seen in structures; therefore, it is necessary to identify them properly in order to get more realistic evaluation of the structure. A review of most of the famous deterioration mechanisms has been focused on in this chapter.

2.1.1 Studies on impact of sea water on concrete

Construction engineers have utilized reinforced concrete structures almost from the beginning of this century for coastal structures. In 1916, a survey of numerous concrete structures along the sea coast of the U.S.A showed that the majority of reinforced concrete structures subjected to action by seawater exhibited evidence of deterioration due to corrosion of embedded steel above the waterline (Finley 1961; Wig and Ferguson 1917). The effectiveness of concrete in preventing reinforced steel corrosion was recognized around 1951 (Hausmann, 1964). The vital factor influencing mild steel performance in a marine environment is the type of exposure, coupled with wind, surf, and salt spray to be entrained and transported to the metal surface, to develop a high corrosion rate. The rate of attack may be affected by rainfall, humidity, temperature, solar radiation, etc., which are predominant factors in a tropical environment (Southwell et al. 1960). The amount of sea salt deposited on the surface decreases rapidly with increasing distance from the sea coast wherein the thickness of the concrete cover is also one such factor to be considered.

The chemical protection offered by the concrete is due to the formation of a protective film of Fe_2O_3 on the steel surface formed in alkaline and aerated solution (Verbeck 1975; Brown and Geoghegan 1979; Cherry and Price 1978). The factors affecting the durability of concrete in the marine environment have been discussed by several authors (Cherry and Price 1978; Cherry and Kashmirian 1983). (Conjeaud 1980; Buenfeld and Newman 1986) had conducted experiments on the surface layers of concrete exposed to marine conditions. The observation showed that mineral layers formed were different from the layers formed in the concrete exposed to freshwater. Accordingly, the first layer formed was of brucite, which was later overlapped by aragonite. Magnesium ions present in seawater lead to the precipitation of aragonite over calcite (Berner 1975).

Conjeaud (1980) observed the presence of brucite layers on the surface of mortar sample at the earliest stage of exposures. The report mentioned variations in the thickness of the brucite layers formed in ordinary portland cement (OPC) mortar samples that were very thick compared with Type V (sulfate resistant) cement mortar samples. This indicated the reduction of calcium hydroxide in those samples. After exposure to samples for two years, an aragonite layer was formed on samples, and the thickness was similar for all types of mortars. This investigation concluded that the combination of a double layer of the minerals (brucite–aragonite) acted as a protective layer for reducing the severe attacks on the cement matrix exposed in the marine environment.

Mechanical strength of the concrete reduces as some minerals like gypsum, calcium chloride, and calcium bicarbonate are soluble in seawater and result in leaching of concrete along with an increase in porosity accompanied by permeability (Glasser et al. 2008; Mehta 1991). Chloride reduces the expansive characteristic of ettringite which will be formed due to the presence of sulfate concentration available in seawater (Mehta 1991). The time till depletion of calcium hydroxide happens till then the formation of brucite will continue. Subsequently, calcium silicate hydrate gets decalcified by magnesium sulfate, converting into magnesium silicate hydrate, a non-binding material of the cement, thus weakening the cement matrix (Bonen 1992).

The factors that govern the drive of pollutants are the substances that get diffused in the pore water and pollutants that get adsorbed into pore walls. This results in hydrodynamic dispersion and convection of substances due to pore water flow (Reinhardt and Jooss 2003). The rate of deterioration of concrete is dependent on the exposure period to harmful chemicals, the concentration of chemicals, and the chemical resistance of concrete (Li and Yang, 2007). Since concrete becomes porous due to these reactions, chloride ions' ingression in seawater may disrupt the passive layer by permitting oxidation near the reinforcing steel areas. Because of this, there will be a considerable change in the volume causing expansion, crack formations, and gradually the matrix of the concrete weakens.

Concrete exposed to the marine environment is subjected mainly to chemical attacks from dissolved salts like sulphates, apart from aggressive ions, which have lower resistivity and promote corrosion (chlorides). Deterioration of concrete is also aided by diffusion. Freezing and thawing, wetting and drying apart from the chemical reactions.

2.1.2 Studies on durability of concrete exposed to marine environment

For modern offshore constructions, the desired properties of the material are often complex, demanding, and occasionally conflicting to some degree, thus requiring the working out of an optimal solution. The concrete for construction in a marine environment like gravity platforms, harbor structures apart from the shoreline, and near-shore structures should have adequate mechanical properties like compressive, tensile, and fatigue strengths, etc. This apart, to ensure durability against the marine environment, the concrete should also have a low permeability to minimize the diffusion of salts, resistance to sulphate attack, and low hydration heat to avoid excessive internal microcracking.

The marine environment, being the most severe of the natural environments, requires more durable concrete to withstand the deterioration of concrete and the corrosion of embedded steel. The types of cement selected should be such that less heat is generated during hydration resulting in improved resistance to cracking during curing. The use of high alumina cement should be avoided in a location where the ambient temperature is likely to exceed 180^0C, even for short durations. This is due to a retrogression in strength and reduced durability (Biczok and Blasovszky 1964).

2.1.3 Effect of cement on concrete used for marine constructions

Cement content plays a vital role in preventing corrosion. An increase in cement content tends to give increased protection (Griffin, 1967). Cement content for adequate protection against corrosion is recommended to be 250 kg/m^3 to 425 kg/m^3, although the most generally recommended minimum value is 360 kg/m^3 to 364 kg/m^3 (Bazant 1979; Veritas 1975). Long-time durability tests of Portland cement concrete in seawater have indicated that cement lowest in C_3A is relatively more durable. A cement of high alkali content would be more desirable because it offers higher pH around the reinforcement (Verbeck 1975). In general, if the pH is maintained throughout corrosion cannot occur even in the presence of the hostile environment of salinity combined with oxygen. This range of pH is called the inhibitive range. Here even if minor cracks may interconnect and reach the surface of the reinforcement and allow the build-up of salinity and oxygen level, this does not damage the steel surface. This may be due to the inhibition provided by the alkalinity present in the crack region. Hydrated cement contains calcium hydroxide, which raises the alkalinity of the concrete to a pH of around 12.5 (Erlin and Verbeck,1975; Szilard and Wallevik, 1975; Browne et al., 1977).

2.1.4 Effect of supplementary cementitious material on concrete

Ongoing progression in concrete technology innovation has revolutionized the mixture of different conventional ingredients to improve the preferred properties of concrete, which have reintroduced its definition. Over the past few decades, efforts towards improving the concrete characteristics have shown that fly ash (FA), a mineral admixture, enhances concrete durability and corrosion characteristics if appropriately utilized.

Studies on the resistance of concrete to sulphates and seawater have confirmed the addition of 15 to 20% slag, FA, or resistance to concrete in the marine environment

(Guyot et al. 1983). The presence of FA in concrete has been found to cause a substantial reduction in seawater attacks due to the reduced permeability and reduced quantity of the available free lime (Ftikos and Parissakis 1985). Up to 25% cement replacement level by mass can be satisfactorily used for structures subjected to marine exposure provided the water to cementations material ratio does not exceed 0.5. (Kumar et al. 1987) noticed that FA reduces the free lime in the process of pozzolanic reaction, which helps in minimizing the formation of 'ettringite', a destructive agent formed in the pores of the concrete. It has also been found that the pore structure of cement paste with FA is less porous, resulting in diminished rates of diffusion of chlorides

Today the application of supplementary cementitious materials has redefined the durability properties offering resistance for chemical attacks susceptible to the marine environment (Neville 1995). Many researchers have reported that the action of pozzolanic materials enhances the sulfate resistance of concrete exposed to seawater (Dongxue et al. 1997; Obla et al. 2003; Mehta and Monteiro 2017). The experimental investigation carried out by (Jau and Tsay 1998) reported that the compressive strength of ordinary concrete decreases after 90 days of exposure to seawater. Still, the strength of slag concrete increases with time. After exposure of specimens for one year corresponding to the sequence of the coefficient of diffusion, the slag concrete has shown a higher potential for corrosion with reduced pore size and pore volume.

2.1.5 Effect of superplasticizers in concrete

A commonly reported statement is that adding mineral admixtures to concrete decreases the flow because of the greater surface area and thus demands more water along with superplasticizers (SP) (Agullo et al., 1999). Mineral admixtures are vital as blended cement will directly influence the microstructure of fresh cement paste, which upsurges yield stress and thereby reduces plastic viscosity (Obla et al., 2003). Researches have been conducted to advance the rheological and mechanical properties by combining various fine particles like BFS, FA, etc., where mineral admixtures have dynamically backed in the improvement of workability in the fresh state and to improve strength characteristics due to their pozzolanic reaction and latent hydraulic properties (Comparet et al., 2003). Several studies have contributed to enhancing the durability properties of concrete, which have helped to modify the pore structure and microstructure by incorporating artificial pozzolana like fly ash etc., to resist chloride and sulfate attacks (Yeau and Kim, 2005).

Unpredicted and detrimental trends like bleeding, rise in setting time, and reduction in cost were noticed by the use of cement and SP, which are incompatible. Before using SP in concrete, the revision on the compatibility issues on cement-SP interaction is necessary. Nowadays, the use of SP has been emphasized in the developing trend of concrete production, which achieves desirable properties in both plastic and hardened state. Flow behavior rules the concrete properties and is measured by the dispersion of particles, as SP results in dispersion into smaller cement particles of coarse agglomerates that are major in the cement paste and concrete mix, intensifying the fluidity (Puertas et al. 2005). The decrease in the w/c ratio improves strength and workability; adding SP will effectively reduce the capillary porosity and permeability. Thus, it helps to decrease the heat of hydration and improve the concreting process in hot climates and marine structures. The porous patches were noticed to be lesser with a decrease in size in heavily superplasticized concrete. SP contributes majorly to increase the workability of mixes and enhancement of compressive strength of concrete (Ramezanianpour et al. 1995; Malagavelli and Paturu 2012). (Palin et al. 2015) studied the autogenous healing capacity of mortars prepared using OPC and GBFS, which were cured in fresh and seawater. OPC specimens immersed in seawater showed higher healing capacity than that of BFS cement mortar specimens. But OPC specimens cured in seawater had a huge compressive strength loss compared to all sets of specimens. The variation in behaviour of these specimens was attributed to the presence of the ions in seawater and the amount of $Ca(OH)_2$ in mortars. A more recent study on the performance of FA concrete environment indicated that concretes containing 0 to 50% FA were more resistant to penetration to chloride ions than ordinary portland cement concretes.

Consequently, corrosion of steel reinforcement was Reduced in FA concrete (Murali 2019). The quantity of cement in the concrete mixture should be sufficient; if not, it will cause insufficient paste volume to surround the aggregates. Reduction in cement reduces the strength and workability, which cannot be overcome with the increase in w/c. Hence, incorporating 350 to 450 kg/m^3 of cement becomes significant, which is the optimum amount of cement content. This usually happens in the case of plain cement. Still, the results have shown that supplementary cementitious materials in the cement have exhibited better workability at constant cement content and w/c ratio, which will attribute to the strength gain in concrete (Huseyin Yigiter et al., 2007). The microstructure of concrete, which is superplasticized moderately and heavily were investigated by (Diamond, 2005) to govern the changes in the patched microstructure of OPC concrete and polycarboxylate ether (PCE) based addition. The studies concluded that the patched structure was observed in both moderately and heavily superplasticized concrete. This increase in the flow is mainly in PCE-based SP because of the rise in the surface potential force the solid-li quid affinity, and the steric hindrance (Sathyan et al. 2018).

2.1.6 Effect of water-cement ratio on concrete

The w/c has an important influence on the quality of concrete since it governs its strength, permeability, consistency, and workability. Furthermore, for a given concrete strength, the w/c prescribes the cement content of the concrete and its alkalinity (Szilard and Wallevik, 1975). The recommended w/c ranges from 0.4 for severe exposure to 0.72 for relatively safe exposure (Friedland 1950; Houston et al., 1972). The most commonly used w/c is between 0.35 to 0.6 as lower and upper limits (Szilard 1969).

2.1.7 Role of aggregates in concrete

Generally, aggregates are inert and constitute 80 to 90% of the mass of concrete. But care has to be taken to avoid the selection of aggregate which are so porous to the environment as to accelerate corrosion of reinforcement (Friedland 1950). The grading of aggregates is as important as the choice of aggregate type in producing dense and impermeable concrete (Houston et al., 1972). A coarse grade of aggregates has low values of effective surface area and permeability to aggressive media. Therefore they provide better protection to the reinforcement in concrete (Szilard and Wallevik, 1975).

River sand is a popular construction material used to produce cement mortar and concrete, widely accepted as the most basic need in mix proportion. This being an important ingredient of concrete, and properties of a particular concrete mixture can be controlled through the extent and amount of river sand used to define concrete. This decides the noteworthy properties like workability, durable properties, mechanical characteristics of concrete. Sand acquires a significant portion of cement in the mix. Since it is fine it fills the pores of concrete, attributing to strength parameters. The change in the volume gets reduced by sand after the setting process and hardening mechanism. It offers a mass of appropriate particles to counter applied loads and exhibit higher durability than paste. The above advantages of sand play a vital role in concrete to harden and gain strength. The utilization of river sand is high due to the enormous use of mortar and cement. Along these lines, the need for sand is more in developing nations to lessen the faster growth of infrastructure (Jain and Pal 1998). The quarrying of large rocks and mountains to produce coarse aggregates has a long-term impact on the environment. Excessive sand mining has exploited the river beds and headed the imbalance in the ecosystem. A well-known fact is that excessive production of minerals has a severe impact on the environment. Deep excavation of the mother earth has led to the plundering of river beds, and the dismount of deposition of sand activities is generating higher impact, blindly compromising the changes in the physical characteristics which are shaving the areas that are naturally covered with comprehensive resources generating particulates.

2.2 NEED FOR NEW ALTERNATIVE MATERIALS

An increase in the demand for aggregates in India is alarming the industries for increasing the production of the same. The consumption of fine and coarse aggregates as per the recent estimate consumed in India was 3330 MT in 2015, and it is expected that the chances of the requirement may rise to 5075 MT by 2020 (World Construction Aggregates, Industry Study with Forecasts for 2017 and 2022) The civil engineering fraternity has been advised to look into alternative aggregates for replacement of conventional total aggregates (coarse and fine) due to restrictions laid by the government regarding mining issues. Thereby, many researchers have been kept in place to investigate the new alternative materials to mitigate the impact on the environment (Kawano, 2002; Ganiron Jr, 2013; Butler and Harrisson, 1998; Saxena and Simalti, 2015; Anderson et al., 2009). According to studies carried out by (Pappu et al., 2007), the solid waste generated in India accounts for 960 MT annually. It includes 290 MT of waste produced by mining and industrial sectors which is unwanted inorganic waste.

Meanwhile, significant expansion is happening for wastes produced by industries as natural resources are being exploited on the other side. With this concern, many initiatives have been taken up to utilize industrial wastes in concrete effectively. Thus, reducing the material cost required for construction activities. The industrial wastes used as a replacement for NFA in the preparation of concrete have added to the better performance and benefits of the environment. This makes the concrete inexpensive and improves the ecological factor by providing a solution for the disposal of these wastes (Bahoria et al., 2013). Alternative materials to be used as NFA to reduce the burden on the environment are being extensively investigated worldwide, and looking to the quantum of requirements, quality, and properties, and there has been a global consensus on the materials. The use of CS, GBFS, SS as an alternative to NFA in cement mortar and concrete has proved beneficial environmentally as well as economically. The incorporation of residues in cement mixture adds to several benefits like the reuse of waste generated from industries, decreases the exploitation of natural resources, and provides a solution for disposal issues. In the present work, CS and PGBS have been used as a partial replacement for NFA to determine the durability of concrete. The maximum allowable limit for replacement of natural fine aggregate by copper slag as per IS 383:2016 is 40% for plain concrete, 35% reinforced concrete and 50% for lean concrete.

2.2.1 Copper slag

Many researchers feel that the ideas on the effective utilization of the CS in concrete, apart from considerable attention in the research, are still limited (Zhu et al., 2012; Wu et al., 2010a; Al-Jabri et al., 2009). CS is a by-product generated during the refining of copper and matte smelting (Davenport et al., 2002). Almost 2.2 to 3 tons of CS slag is produced during the production of one ton of copper (Gorai and Jana, 2003). An estimation noted that 24.6 million tons of CS slag are produced worldwide by the copper industries (Gorai and Jana, 2003; Burger, 2018). Today the CS is used as a partial replacement for NFA and coarse aggregates (CA) in concrete which has a significant impact on mechanical as well as durability characteristics of mortars and concrete.

The quantity of CS generated annually throughout the world is around 33 MT, including about 6 to 6.5 MT contribution by India. To achieve specific properties required for better performance of mortars and concrete, it is recommended to use 50% of CS as a replacement for NFA (Sankh et al., 2014; Al-Jabri et al., 2009; Al-Jabri et al., 2011) have measured the influence of using CS as a substitute for sand on the characteristics of high strength concrete and other concrete properties. The physical and chemical properties of CS are similar in the size range of sand granular in nature and black glassy particles. The bulk density of granulated CS varies from 1.9 to 2.15 g/cc. CS has available free moisture content to be less than 0.5% and the silica presence of about 26%, which is necessary as it is the principal constituent of the river sand applied in normal concrete production.

Also, the CS aggregates have a better compressibility feature than sand, which has partially lessened the concentration of stresses (Al-Jabri et al., 2011). It was determined that compressive strength enhanced by supplanting NFA by 40% of CS (Al-Jabri et al., 2009; Al-Jabri et al., 2011; Sudarvizhi and Ilangovan 2011; Chavan and Kulkarni 2013; Ambily et al. 2015; Velumani and Nirmalkumar 2014; Poovizhi and Kathirvel 2015; Wu et al. 2010b). The blast furnace slag is a dark smooth particle and granular (Sankh et al. 2014). CS is dark granular particle which will be polished and has a grain size gradation like natural sand (Ambily et al., 2015). According to Sankh et al. (2014), the gradation obtained after sieve analysis of CS resulted that around 75% of particles were within the range of 1.18 to 0.3 mm. According to (Ambily et al., 2015), the specific gravity of CS was 3.37 and bulk density variation from 1900 kg/m^3 to 2150 kg/m^3.

Al-Jabri et al. (2011) noted 0.17% water absorption capacity, and the slag contains about 53.45% of Fe_2O_3. However, Ambily et al. (2015) specified water absorption capacity would range between 0.30 and 0.40% in CS aggregate. CS samples were subjected to leaching tests of heavy metals, which comprises the sample treated under an aggressive environment. The results exhibited that the heavy metals after leaching was less than the toxicity limits even under aggressive conditions. This showed that CS is non-hazardous and non-reactive material. This has been approved in the United States and by the Basel Convention for import and export internationally (Alter, 2005). Even though CS has a minimum presence of heavy metal, leaching studies conducted under aggressive conditions have shown that these values are below toxicity limits (Supekar, 2007). As per British standards to be used as an aggregate and filler, the chloride and sulfate contents in CS are within limits. As per the review obtained from (Shi et al., 2008), many standards have recommended CS as aggregate in South Korean (KSF2543, 2004), Japanese (JISA5011-3, 2016), and Indian Standard (IS:383-2016). The building construction authority of Singapore (BCA) in 2008 has also approved rules for the usage of CS as a sustainable material for use as a recyclable material (Hwang et al., 2013).

Workability plays a vital role in the design mix that is majorly dependent on the behavior aggregates. (Hwang and Laiw 1989) stated that bleeding observed in the case of CS mortars was less when compared to the control mix. But it was noted that the heavyweight and glassy surface of irregular particle shape of CS granules are the major reason for bleeding in mortars. Also, greater resistance for abrasion was noticed in the case of CS mortars (Tang et al., 2000). Also, Hwang and Laiw (1989) assessed compressive strength development in mortars and concrete comprising fine CS aggregate with various w/c ratios. The results showed that mortars with a large CS volume achieved low early strength at w/c of 0.48. But the mixtures with 20 to 80% replacement of NFA by CS had attained higher strength than that of control mixtures. A similar trend was notified in the compressive strength gain of concrete. Resende (2008) reported the use of blasted CS in mortar as an aggregate, replacing river sand. The presence of a higher amount of iron and zinc oxides and sulphur traces reduced mechanical indexes, reaching an optimal value of replacement of 25%, though it had similar physical properties.

Al-Jabri et al. (2009) evaluated that as the CS amount increases the workability of concrete is also enhanced. The slump of the control mix measured was 28 mm, while the concrete with 100% replacement for NFA achieved 150 mm. (Wu et al. 2010a) identify that this increment in workability for CS concrete was due to the composition of smooth surface, which appears like a polished particle and lower moisture absorption characteristics of the slag aggregate. Concrete incorporating CS helped to decrease surface water absorption. Thus, improved workability and substantially improved mechanical properties irrespective of grades of concrete (Khanzadi and Behnood 2009; Ambily et al., 2015). The density of concrete determines the workability of concrete. CS had shown increment in density compared to the control mix as reported by Al-Jabri et al. (2009), which attributed to the higher specific gravity of CS aggregate. The same perception can be compared with the studies which stated that an increase in the amount of CS aggregate increases the density of concrete according to Poovizhi and Kathirvel (2015). The strength of concrete depends on the behaviour of aggregates in the concrete mix.

In concern with geotechnical properties of CS showed that it was non-plastic material. Meanwhile, the permeability and consolidation properties of CS were similar to an NFA that can be used successfully to construct retaining walls, sand compaction piles, and embankments (Bharati and Chew, 2016; Prasad and Ramana, 2016; Shahiri and Ghasemi, 2017). The primary purpose for the usage of CS in concrete is because it is a non-reactive, non-hazardous granular material of normal sand-size fraction and its chemical properties (chloride and sulfate content) lie within permissible limits for the durability of concrete (Gorai and Jana, 2003; Pappu et al., 2007; Dash et al., 2016; Mavroulidou, 2017). Ayano and Sakata (2000) reported a difference in the size of the particle of CS shows the different setting times as smaller the size of CS leads to an increase in the setting time. The high hardness and better mechanical properties of CS have found their application in concrete pavements. Bleeding is one of the important parameters to take care of as it affects the durability of concrete.

Shoya et al. (1997) observed that w/c, air content, and volume fraction decide the rate of bleeding for CS concrete. The possibility of bleeding can be reduced by limiting the use of a percentage of CS in concrete up to 40%, which will regulate the volume of bleeding to a lesser amount of 5 lt/m^2. As per the studies, the compressive strength of concrete was more than the reference mix up to 50% replacement and there was a decrement due to the availability of free water which was more than the sufficient amount of water required for hydration. As a result, there was a fall in compressive strength for further replacement. This unbelievable increase in strength was due to implementing a static slump by lessening the amount of water as CS replacement level increased (Al-Jabri et al., 2009). Wu et al. (2010a) carried out the investigation and concluded that the utilization of 40% of CS as a substitute for NFA contributes to high strength properties in concrete.

Brindha and Nagan (2011) investigated concrete by partially replacing NFA with CS from 0 to 50% (variation of 10% range). The results exhibited that compressive and tensile strength increased by 40% and 35% and recommended using CS up to 50%. The opinion was also matched by Poovizhi and Kathirvel (2015), as they also showed a significant increase of compressive strength for 40% partial replacement of NFA by CS. The compressive and tensile strength with CS observed was high when compared to control concrete (Caliskan and Behnood, 2004; Najimi and Pourkhorshidi, 2011; Chithra et al., 2016). According to Al-Jabri et al. (2009) splitting tensile strength was higher for concrete having 20%, 40%, and 50% of partial replacement of CS for NFA but found a reduction in splitting tensile strength for 10%, 60%, 80%, and 100% of NFA when replaced by CS. It was observed that CS concrete mix up to 80% had achieved better splitting tensile strength. (Wu et al., 2010b) also found reduced splitting tensile strength, whereas for NFA when replaced by 40% with CS and NFA replaced by 20%, 60%, 80%, and 100%, the strength of concrete mixes was comparatively more than control mix.

Arivalagan (2013) observed a significant improvement in concrete with CS as NFA showed that flexure strength of beam increased by 21 to 51% for CS concrete beam with the increase in energy absorbing capacity. Since the water absorption capacity of CS is less more the amount of replacement leads to segregation and bleeding of concrete. (Hwang and Laiw 1989; Ayano and Sakata 2000) reported that shrinkage of concrete specimens got reduced with the introduction of CS as NFA when compared to the control mix. (Al-Jabri et al. 2009) examined that an increase in CS percentage in the case of HPC increased the density up to 5% along with the increment in workability. The partial replacement of CS for NFA up to 50% yielded better results than the control mix. Results showed that up to 40% replacement of NFA with CS marked no changes in load failure of the column.

No significant sulfate attack was observed along with less rate carbonation when CS was evaluated as a replacement for aggregate in concrete (Hwang and Laiw 1989;

Ayano and Sakata 2000). Some researchers stated that CS concrete exhibited lower resistance for freeze and thaw attacks than control specimens (Shoya et al., 1997; Shoya et al., 2003). The other research works also conveyed similar results or better resistance for specimens made with CS concrete partially replaced with NFA.

The chloride penetration value of CS concrete as per ASTM C1202 was graded under the category "very low". This shows that lesser ingression of ions to CS concrete reduced the pore structure and made the concrete impermeable. The specimens exposed for the acid resistance test showed that CS concrete was less resistant to H_2SO_4, but the results were almost similar to control mix specimens (Brindha and Nagan 2011). The guidelines for using CS as NFA in mortars and concrete have been published by China (SPCSA, 1999). Since concrete is composed of 70% volume of aggregates, considering the protection of the environment CS is declared as safe material, not a harmful waste based on criteria of different standards. Furthermore, the effective utilization of CS in concrete adds on to the technical benefits for all industries concerned with its usage. But consideration is required to evaluate the economy of CS application (Shi et al., 2008). Typical compaction characteristics of copper slag in terms of Maximum Dry Density (MDD) and Optimum Moisture Content (OMC) indicated insensitiveness of dry density with moisture content which is an added advantage for field construction. Slope stability of copper slag embankment depends on its shear strength characteristics. High angle of internal friction justifies its suitability in embankment construction. Permeability characteristics of copper slag play a key role in the development of pore water pressure (pwp) when used in embankment construction. Permeability values indicate the good permeability characteristics similar to conventional sand and the pore water pressure would be dissipated easily when used in embankment construction. The increase in density of concrete due to use of copper slag and steel slag aggregates need to be taken into consideration in the design of structures. Copper slag having higher specific gravity (up to 3.8) shall be permitted for part replacement of aggregates in accordance with (4.2.1, IS 383:2016), such that the average specific gravity of the fine aggregate is not more than 3.2.

From past researches it is observed that, the compressive strength and flexural Strength is increased due to high toughness of copper slag. Replacement of up to 40% of FA with CS caused no major changes in column failure load increasing the ratio of CS to NFA reduced the concrete strength and column failure load, and increased concrete slump and lateral and vertical deflections. Compressive strength and split tensile strength have shown that copper slag is superior to corresponding control concrete the corrosion rate of copper slag admixed uncoated rebar is somewhat higher when compared to controlled specimens. But when the rebar is coated with zinc phosphate paint the corrosion rate had become zero. A significant increase in the compressive strength for up to 90 days of hydration. Also, a decrease in capillary porosity and an increase in gel porosity. Addition of copper slag to concrete results in an increase on the concrete's axial compressive, splitting tensile strength and decrease in the absorption rate by capillary suction, carbonation depth and hence improved its durability. The wall constructed with copper slag backfill showed lesser faces deformations compared with sand. Durability characteristics such as resistance of freeze–thaw and abrasion were improved. The effectiveness of copper slag replacement in improving the concrete resistance against sulphate attack

2.2.2 Processed granulated blast furnace slag (PGBS)

Today the steel slag from steel industries try to fulfill the supply and demand gap to meet the construction requirements as per the standards; steel makers have adopted new processing techniques to produce the slag considering environmental protection and economic aspects. In this regard, an initiative was driven to introduce processed granulated blast furnace slag as an eco-friendly alternative material for river sand by the team of JSW in India. Granulated blast furnace slag (GBFS), obtained from rapidly water-cooled slag from blast furnace during the manufacture of pig iron. The presence of lime content in the material has resulted in inefficient use of concrete production. Yüksel et al. (2006) focused on using non-grounded GBFS in concrete as a replacement for sand. The gradation obtained after GBFS grain size sieve analysis had 62% particles ranging between 1.18 and 0.10 (Bilir et al., 2017). The loose bulk density and compacted bulk density of the GBFS was 1052 kg/m^3 and 1236 kg/m^3, respectively (Yüksel and Bilir, 2007; Yuksel and Genç, 2007). According to Bilir (2012), water absorption of GBFS was 10.0%. The primary chemical component of GBFS was CaO which was 56.10%. In the case of GBFS, the same behaviour was observed as the replacement percentage of GBFS increases the compressive strength of concrete decreased (Yüksel et al. 2006). The slump measured was 100 mm for 50% replaced GBFS aggregates, whereas the reference mix had achieved 60 mm (Yuksel and Genç 2007).

The studies on GBFS as a fractional substitution of NFA was carried out, and the researchers resulted that at early age concrete substituted with the slag showed a comparable compressive strength, nevertheless at 365 days, the more the amount of NFA supplanted by slag, the greater the compressive strength of concrete (Yüksel et al. 2006; Yüksel and Bilir 2007; Yüksel et al. 2011; Yuksel and Genç 2007). For GBFS concrete, splitting tensile strength and flexure strength decreases with an increase in the substitution of slag aggregate (Yuksel and Genç 2007). At an early age, the strength of GBFS concrete will be similar to the reference mix. As the curing period increases the reactivity of slag and an increase in slag, substitution achieves better strength than reference concrete (Valcuende et al., 2015). GBFS that was available as a replacement for NFA for decades failed to satisfy the requirement of construction activities. However, it had all properties similar to NFA -like inert, non-toxic, and free from traditional impurities and matched the chemical compositions of an aggregate. Several tests carried out resulted in exhibiting dissimilarity concerning the physical properties required for aggregate as per the specifications.

Many researchers have been carried out using GBS as a replacement for river sand in mortars and concrete. Still, it was restricted for partial replacement between 50 to 75 % only as of the quality of the material varied depending on the sources. The major highlight was that slags to act as a replacement for aggregate should have a sufficient density of less than 1400 kg/m^3. In contrast, the bulk density of river sand varied from 1300 to 1600 kg/m^3, and also specific gravity must be less than 2.5 as per standards to satisfy the weight required for making of cubic meter of concrete. But many studies showed that the density of GBFS range from 950 to 1100 kg/m^3 with high water absorption and lower specific gravity, which reduced the properties along with the irregular, flaky shape and porous nature with sharp edges in the particles became a prime reason for reduction of strength in concrete with the rise in quantity.

These identifications were focused on improvising the property of GBFS and led to the development of new processing techniques for converting GBS to processed granulated blast furnace slag (PGBS) in an acceptable form of NFA (Nadeem and Pophale 2013; Jain and Pal 1998; Gonçalves et al. 2007). Based on the new processing techniques and several trials carried out for improving the drawbacks, GBFS resulted in the production of PGBS. This slag showed an increment in specific gravity, bulk density, and structure of the particles. Reduction in the porosity of slag granules and made the structure denser improved the bulk density close to 1500 kg/m^3 and water absorption decreased from 8% to less than 3%. The shape of the particles developed as blunter edges, and the physical properties satisfied the requirements similar to river sand. The performance of PGBS was equally good in terms of flow characteristics, and compressive strength was also higher than the cement matrix with river sand. The construction economy was considered to produce the low-cost, eco-friendly aggregate with good quality and made available throughout the year. Today, PGBS has found applications in roads, highways, and building construction (Kumar et al., 2016).

2.3 SUMMARY OF PAST INVESTIGATIONS

Concrete is prone to disintegration when subjected to the marine environment due to the various deleterious ions present in seawater as seawater consists of sodium, chloride, calcium, magnesium, and potassium ions as major chemical constituents. Revolution in concrete mixes with the introduction of new alternative materials as a replacement for concrete constituents has increased the durability of concrete exposed to aggressive environments.

From past research, it is investigated that the slags incorporated in concrete have shown better performance in mechanical and durability aspects. Structures exposed to the marine environment are usually prone to many deteriorations of concrete and structural-related problems. The performance of a ground blast furnace slag concrete against seawater attack results in specimens having higher seawater attack resistance than that of the reference concrete. This improvement can be explained partly by the decrease in the permeability of the specimen and partly by the seawater resistance of the additives.

CS finds a potential application in concrete for marine application; there was an increase in compressive strength, flexural strength, and reduction in sorptivity and chloride ion penetrability values. The addition of fly ash enhances the pozzolanic reactivity, thereby improving ITZ (Inter transition Zone), forming a compact microstructure resulting in strength enhancement. Many research works had shown better durability performance of concrete exposed to the marine environment when slags were partially replaced as the binder. But not much work was identified to understand the durability performance of slag when it was used as an NFA replacement and exposed for seawater curing.

This finds a research gap to investigate the effects of using CS and Processed Granulated Blast Furnace slag (PGBS) as a replacement for fine aggregates in concrete in terms of durability aspects as extensive studies have been made with a conventional fine aggregate of river sand, what is it with others? It will be studied to develop suitable concrete to overcome the effects when immersed in seawater with primary concern to achieve a sustainable environment.

This research aims to understand the seawater effect on concrete containing CS and PGBS as fine aggregates. For this, concrete specimens containing various replacement levels of slag aggregates (0 to 50%) were cured in fresh and seawater for up to 365 days. The compressive and splitting tensile strength development and the ingression of chloride, sulphate, and sodium ions are examined at different ages after curing in both fresh and seawater. The ingression of ions is examined using the toxicity characteristic leaching procedure (TCLP) method. Further, microstructural investigations are carried out using a scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS) analysis to understand the phase changes and the pore structure of CS and PGBS concrete when cured in seawater.

2.4 PROBLEM IDENTIFICATION

Considering the structural design aspect, compressive strength is the first-order parameter in good concrete, usually used to estimate concrete quality. The importance of concrete durability is more accepted currently, which represents a significant consideration in structural design. The selection of aggregates plays a vital role in the mix proportion of concrete. So, this finds a research gap to investigate the effects of using CS and processed granulated blast furnace slag (PGBS) as a replacement for natural fine aggregates (NFA) in concrete in terms of durability aspects as extensive studies have been already made with the conventional fine aggregate of river sand. It will be studied to develop suitable concrete to overcome the effects when immersed in sea water with major concern to achieve a sustainable environment.

2.5 AIM AND OBJECTIVES

The present investigation aims to study the properties of slag-induced concrete concerning the effects of CS and PGBS as a partial replacement for NFA in concrete when exposed to an aggressive environment.

2.5.1 Objectives

- ➢ To determine the effect of slag aggregates and superplasticizers on cement paste, cement- sand mortars, and concrete.
- ➢ To determine the effect of chloride, sulphate, and sodium ions on slag-based concrete exposed to marine water.
- ➢ To determine the role of salinity, temperature, and pH of seawater on the durability of slag-based concrete.
- ➢ To develop suitable concrete by incorporating slag for the marine environment.

2.5.2 Scope

- Concrete is being used as construction material for ports, harbours, and shore protection works. Due to its ability to resist weathering action, chemical attack, and other deterioration processes, it is an excellent material for coastal construction.

- This research will be carried out for the effective utilization of slags in concrete exposed to the marine environment, which is significant in finding alternatives for natural sand.
- Study of degeneration of concrete due to the immersion of concrete in seawater.
- Microstructure studies of concrete samples exposed marine conditions to understand the effect of slag in concrete.

2.6 CLOSURE

The review from the past works confirms that due to the increase in construction, the industry is facing great challenges to serve the two pressing needs of human society, namely environmental protection and trying to meet the infrastructure requirement of our growing pollution and consequential needs of urbanization and industrialization. The cement and concrete industries are now slowly becoming aware of the environmental and other sustainable development issues. The mindset of people has been changed due to the emission of the host of greenhouse gases from industrial processes and its adverse impact on climate resulted from the mass-production, mass-consumption, and mass-waste society of the past to a zero-emission society with emphasis on the utilization of industrial wastes and conservation of natural resources.

Also, the factors affecting the durability of concrete in the marine environment have been discussed by several authors. The concrete for construction in a marine environment like gravity platforms harbours structures apart from the shoreline and nearshore. Such structures should have adequate mechanical properties like compressive, tensile, and fatigue strengths, etc. This apart, to ensure durability against the marine environment, the concrete should also have a low permeability to minimize the diffusion of salts, resistance to sulphate attack, and inadequate heat od hydration to avoid excessive internal microcracking. Thus, there is a need to streamline and get into a direction where the challenges are addressed through the professional approach. The approach should be scientific. The proposed alternative technologies, which offer safe, durable, energy-efficient, economical, and environment–friendly green dwellings to our countrymen, are recommended to be encouraged for wide-scale application.

CHAPTER 3

MATERIALS AND METHODOLOGIES

3.1 GENERAL

Concrete is a well-known load-bearing material. Therefore, attention has been focused on its mechanical properties, especially its strength. It seemed to be its cardinal property so that the recommendation for selecting concrete is based upon its strength. But with time, it has been realized that the concrete is not an inert material immune to the environmental conditions to which it is exposed. There are chemical and physical interactions that significantly affect the durability and hence on the service life of the concrete.

Many structures deteriorated much before the stipulated time, causing a lot of economic damage and public inconvenience. High-strength concrete may or may not be high-performance material. So, the selection of materials and methodology adopted plays a vital role in determining the strength and durability of concrete.

3.2 MATERIALS USED FOR THE PRESENT STUDY

The materials used in the presents study constitutes of OPC and PPC as a cementitious material, river sand as a natural fine aggregate, copper slag, and processed granulated blast furnace slag as a partial replacement for natural fine aggregate, coarse aggregates, and superplasticizers to improve the workability of concrete.

3.2.1 Ordinary Portland Cement (OPC)

In the present work, commercially available 53 grade OPC conforming to IS:12269-1987 has been used. The physical properties of the cement obtained are shown in Table 3.1, and the tests were carried out as per IS: 269-4831 and the corresponding requirements as per IS: 12269-1987.

Table 3.1 Physical properties of OPC.

Sl. No	Properties	Obtained Values	Requirements as per IS: 12269-1987
1	Specific Surface area	330 m^2/kg	Not less than 300 m^2/kg
2	Fineness	2.5%	Not more than 10%
3	Soundness	2 mm	Not more than 10 mm
4	Setting Time		
	Initial	68 min	Not less than 39 min
	Final	250 min	Not more than 600 min
5	Standard Consistency	31%	Not specified
6	Specific Gravity	3.10	Not specified

3.2.2 Portland pozzolana cement (PPC)

The physical properties of PPC are represented in Table 3.2. Commercially available PPC conforming to IS: 1489-1991 has been used. The physical properties of the cement were obtained by conducting relevant tests as per IS: 269- 4831 and the corresponding requirements as per IS: 1489-1991.

Table 3.2 Physical properties of PPC

Sl. No	Properties	Obtained Values	Requirements as per IS: 1489-1991
1	Specific Surface area	340 m^2/kg	Not less than 300 m^2/kg
2	Fineness (%)	1.9	Not more than 5%
3	Soundness	1 mm	Not more than 10 mm
4	Setting Time (min)		
	Initial	64 min	Not less than 30 min
	Final	246 min	Not more than 600 min
5	Standard Consistency (%)	31	Not specified
6	Specific Gravity	2.85	Not specified

3.2.3 Fine aggregates

Our Civilization is literally built on sand. Apart from water and air, humble sand is the natural resource most consumed by human beings. Cost variation of natural sand used as fine aggregate in concrete increased construction cost in the past decade. Alternative materials to be used as fine aggregate to reduce the burden on the environment and are being extensively investigated worldwide. There has been a global consensus on materials regarding the quantum of requirements, quality, and properties. The mindset of people has been changed due to the emission of greenhouse gases from industrial processes and its adverse impact on climate resulted from the mass-production, mass-consumption, and mass-waste society of the past to a zero-emission society with emphasis on the utilization of industrial wastes and conservation of natural resources.

3.2.3.1 Natural River sand (NFA)

Sand is small, loose grains of rock and other complicated stuff made by glaciers grinding up stones, oceans degrading seashells, and even by volcanic lava chilling and shattering upon contact with air. In the construction industry, river sand is the most preferred aggregate for the preparation of mortar and concrete. The standard terminology used for sand is fine aggregate. Aggregates shall comply with the requirement of IS 383-2016. Natural sand is a fine aggregate resulting from the natural disintegration of rock deposited by streams or glacial agencies.

In the present work, clean, dry natural sand passing through 4.75 mm sieve and retaining on 75mm IS sieves have been used. Table 3.3 shows the results of sieve analysis obtained for river sand, and it confirms Zone II as per the specifications of IS: 383-2016. The physical properties of the natural fine aggregates are shown in Table 3.8.

Table 3.3 Sieve analysis of natural fine aggregate

IS Sieve Size in mm	**Cumulative Percentage**		**Specification as per IS:383-2016 (Percentage Passing)**		
	Retained	Passing	Zone I	Zone II	Zone III
4.75 mm	1.60	98.40	90-100	90-100	90-100
2.36 mm	8.34	91.66	60-95	75-100	85-100
1.18 mm	26.91	73.09	30-70	55-90	75-100
0.6	49.91	50.09	15-34	35-59	60-79
0.3	79.76	20.24	5-20	8-30	12-40
0.15	99.24	0.76	0-10	0-10	0-10

3.2.3.2 Copper Slag (CS)

Figure 3.1 The copper slag

CS used in the present work is shown in Figure. 3.1and Table 3.4 represent the results obtained from the sieve analysis of CS aggregate. Sterlite Industries India Limited (SIIL), Tuticorin, Tamil Nadu, is a leading producer of copper in India, pioneered the manufacturing of copper, and established India’s largest copper smelting and refining plant for the production of world-class refined copper. It produces CS during the manufacture of copper metal. Currently, about 2600 tons of CS are produced per day and a total accumulation of around 1.5 million tons. This slag is presently being used for many purposes. It is a glassy granular material with sizeable specific gravity particle sizes. The size of the particle is of the order of sand and can be used as an NFA in concrete (Chinmay et al., 2015). The specific gravity and water absorption for CS and sand were determined as per IS: 2386 – 1963 (P-III). Tests to determine specific gravity and water absorption for CS and sand were carried out as per ASTM C128. The leaching studies on CS were determined by (Shanmuganathan et al. 2008). It was found that heavy metals present in CS will not leach even under repetitive acid rain in a natural environment. The major concentration of all elements was well below recommended within limits in USEPA 40CFR Part 261. The physical properties of CS are tabulated in Table 3.8.

Table 3.4 Sieve analysis of copper slag (CS)

IS Sieve Size in mm	**Cumulative Percentage**		**Specification as per IS:383-2016 (Percentage Passing)**		
	Retained	Passing	Zone I	Zone II	Zone III
4.75 mm	0	100	90-100	90-100	90-100
2.36 mm	1	99	60-95	75-100	85-100
1.18 mm	13.9	86.1	30-70	55-90	75-100
0.6	47.9	52.1	15-34	35-59	60-79
0.3	79.7	20.3	5-20	8-30	12-40
0.15	92.7	7.3	0-10	0-10	0-10

The chemical composition of CS is represented in Table 3.5

Table 3.5 The chemical composition of copper slag (CS)

Sl. No	Chemical component	Chemical component (%)
1.	SiO_2	25.82
2.	Fe_2O_3	67.27
3.	Al_2O_3	0.21
4.	Cao	0.13
5.	LoI	6.55
6.	Mn_2O_3	0.21
7.	SO_3	0.10
8.	CuO	1.10

3.2.3.3 Processed granulated blast furnace slag (PGBS)

Figure 3.2 Processed Granulated Blast Furnace Slag

The PGBS used in the present study is represented in Figure. 3.2 and Table 3.6 presents the results obtained from sieve analysis of PGBS aggregate. The PGBS was similar to the true river sand. The size distribution of the processed granulated slag was also identical to river sand. The PGBS matched the required physical properties of fine aggregate to be used in concrete. In addition to properties, the key advantage of slag sand over river sand is the absence of impurities like clay and silt (Kumar et al., 2016).

The chemical composition of the PGBS is tabulated in Table 3.7, and the physical properties PGBS are tabulated in Table 3.8.

Table 3.6 Sieve analysis of processed granulated blast furnace slag

IS Sieve Size in mm	**Cumulative Percentage**		**Specification as per IS:383-2016 (Percentage Passing)**		
	Retained	Passing	Zone I	Zone II	Zone III
4.75 mm	0	100	90-100	90-100	90-100
2.36 mm	0.9	99.1	60-95	75-100	85-100
1.18 mm	14	86	30-70	55-90	75-100
0.6	47.6	52.4	15-34	35-59	60-79
0.3	79.4	20.6	5-20	8-30	12-40
0.15	92.4	7.6	0-10	0-10	0-10

Table 3.7 The chemical composition of PGBS

Sl. No	**Chemical component**	**Chemical component (%)**
1.	SiO_2	33.55
2.	FeO	1.58
3.	Al_2O_3	20.11
4.	Cao	35.41
5.	MgO	8.02
6.	SO_3	0.16
7.	LOI	0.16

The physical and chemical properties of CS and PGBS was provided by the manufacturing companies during the procurement and it is mentioned in Table 3.8.

Table 3.8 The physical properties of the NFA, CS, and PGBS

Physical Properties	**NFA**	**CS**	**PGBS**
Particle shape	Irregular	Irregular	Irregular
Colour	Brownish yellow	Black & glassy	Grey
Type	River sand	Air cooled	Slag granulation
Specific gravity	2.62	3.65	2.5
Voids (%)	33	43	
Bulk density (g/cc)	1.71	2.08	1.5
Fineness modulus	2.7	3.47	2.7
Angle of internal friction	45°	51° 20’	45°
Ultimate shear stress (kg/cm^2)	0.299	0.4106	0.229
Water absorption (%)	1.25	0.3	2.55
Moisture content (%)	0.5	0.1	0.6

Figure 3.3 shows the grain size distribution of the NFA, CS, and PGBS compared to Zone II limits. The sieve analysis of NFA, CS, and PGBS used in the present work satisfies Zone II limits requirements as per IS: 383-2016.

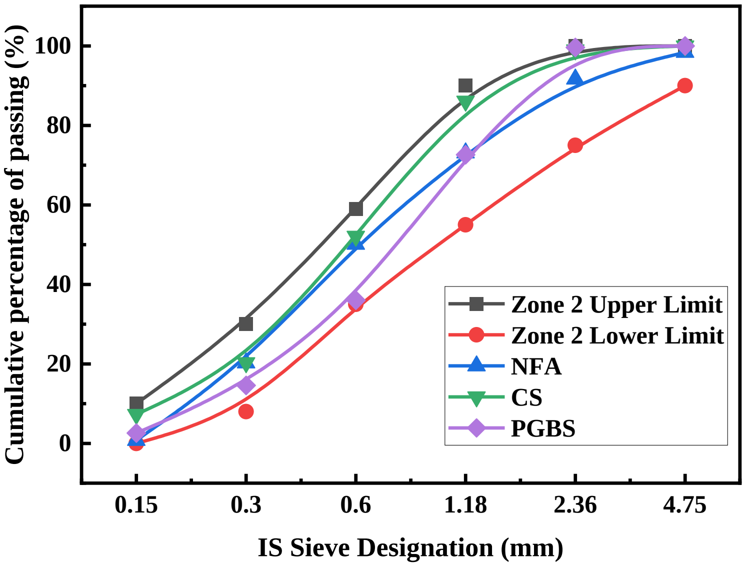


Figure 3.3 Sieve analysis of fine aggregates

3.2.4 Coarse Aggregate

Crushed granite of 20 mm maximum size and retained on sieves have been used as coarse aggregate. Two different sizes of coarse aggregates were used 55% of aggregates are 20 mm passing 16 mm retained and 45% coarse aggregate 16 mm passing, and 12.5 mm retained sieve was used. Table 3.9 shows the physical properties of coarse aggregates used in the present work.

3.2.5 Water

Clean potable water was used for mixing and curing concrete available at NITK, India. Specimens were immersed inside the sea closer to the NITK campus for curing the concrete specimens. Water analysis test was conducted for the nearby sea water samples to understand the variation in the chemical characteristics of water. The result of the water analysis is mentioned in Table 3.10

Table 3.9 Basic test results of 20 mm down size coarse aggregates

Sl. No	Description	Result	Range
1	Shape	Angular	
2	Bulk Density a) Loose b) Compact	1287.72 kg/m^3 1417.69 kg/m^3	Not specified
3	Specific gravity value [as per IS: 2386 (part III)- 1963]	2.74	Not specified
4	Fineness modulus	6.9	Not specified
5	Water absorption [as per IS: 2386 (part 3)- 1963]	0.7%	Not specified
6	Aggregate crushing value [as per IS: 2386 (part IV)- 1963]	23.8%	Not exceed 30%
7	Aggregate abrasion value [as per IS: 2386 (part IV)- 1963]	25%	Not exceed 30%
8	Aggregate impact value [as per IS: 2386 (part IV)- 1963]	26.5%	Not exceed 30%

Table 3.10 Water analysis

Water sample	**pH**	**Conduc-tivity**	**Dissolved Oxygen (mg/l)**	**Alkalinity (mg/l)**	**Chloride (mg/l)**	**Sulphate (mg/l)**	**Sodium (mg/l)**
Fresh water	5.53	84.2 µs/cm	6.68	95.35	15.68	9.5	6.44
N.I.T.K sea water	7.83	25.8 ms	5.67	200	18828.61	1.41	27.23
Sasihitlu sea water	7.75	24.8 ms	5.40	210	18926.17	1.53	28.30

3.2.6 Superplasticizers (SP)

The most important role of SP is to reduce the water: cement ratio. SP's classification and testing methods are based on IS 9103, ASTM C-494, and ASTM C 1017. Apart from reducing water mixing, SP has various functions such as slump retention, set retardation or acceleration, and more. Each type needs to meet different criteria specified in the test specification. In this study influence of water, the reduction will be studied using three different types of superplasticizers, and they are as follows:

- Lignosulfonate (LS) based SP.
- Sulphonated Naphthalene Formaldehyde (SNF) based SP.
- Standard PCE-based SP.

The specifications of the superplasticizers are tabulated in Table 3.11.

Table 3.11 Specifications of superplasticizers

Sl	The chemical name of SP	Brand name of SP	Relative Density	pH	Chloride ion content (%)	Standard code
1	Lignosulfonate (LS)	Pozzolith 102				
2	Sulphonated Naphthalene Formaldehyde (SNF)	Rheiobuild 1125	1.24	≥6	<0.2	ASTM C494 Typ En934-2 T11.1/11.2 G IS9103
3	Poly Carboxylate Ether (PCE)	Master Glenium sky 8233	1.08	≥6	<0.2	ASTM C494 Type F En934-2 T3.1/3.2 IS9103:1999 IS2645:2003

3.3 EXPERIMENTAL METHODOLOGY

3.3.1 Fresh and hardened properties of cement paste, mortars, and concrete

To determine the behaviour of the aggregates all the mixes that were prepared was tested in both fresh and hardened state.

3.3.1.1 Marsh Cone Test

The Marsh Cone test evaluates fluidity and the ideal SP dosage in the case of cement mortar. The pastes were prepared using a 5 L (1.32 gal.) Hobart type blender with a B-type flat beater, with a mixing procedure that produces pastes comparable to those of concrete (Jayasree and Gettu 2010). The mixing sequence adopted for the study was as follows: the cement and 70% of mixing water were mixed at low speed (with a shaft speed of 139 rpm, and planetary speed of 61 rpm) for 1 minute; the superplasticizer and remaining water were then added and mixed for 2 minutes. The mixer was then stopped, and the sides of the bowl and blades were scraped (15 to 20 seconds). The paste was again mixed for 2 minutes at medium speed (with a shaft speed of 285 rpm, and planetary speed of 125 rpm). The Marsh cone test was used to determine the optimum dosage of superplasticizer and to evaluate the flow behavior of cement paste. The apparatus used here consists of a hollow metal cone with an opening of 8 mm (0.31 in.) diameter at the bottom (as per European Standard EN 445 2007). Cement slurry was prepared with the w/c of 0.35 for both OPC and PPC by varying admixture dosage from 0.2 to 2%. A reference volume of 1000 mL (0.26 gal.) of cement paste is poured into the Marsh cone, and the time for 500 ml (0.13 gal.) to flow out is determined.

The fluidity is reflected by the flow time—the longer the flow time, the lower the fluidity. The logarithm of flow time is plotted against the sp/c dosage. The saturation point is taken as the dosage beyond which any further addition of superplasticizer does not significantly increase the fluidity. In this study, the saturation dosage is taken as the dosage corresponding to the point where the flow time versus sp/c dosage curve takes an angle of 140 ± 10 degrees, as proposed by Gomes et al. (2001).

3.3.1.2 Flow table test

Figure 3.4 Flow table test of mortars

Figure 3.4 shows the flow table test of mortars. The blending sequence for preparing the mortar was adopted based on the literature as suggested (Jayasree and Gettu 2010). The fluidity of the mortars was determined using the flow Table test (by measuring the spread diameter) according to IS:1727-1967. A flow table of diameter 300 mm with a mould of 40 mm internal diameter on the top end and 90 mm height was used in this study. The cement mortars were made for 1:3 by weight of cement, and NFA proportion was blended using Hobart blender.

CS and PGBS were fused as a partial replacement NFA at 0 and 50% replacement levels considering the maximum allowable replacement percentage levels as mentioned in IS: 383-2016 to recognize the flow behaviour of CS and PGBS in mortars. Dosages of SP, w/c ratio were altered, laterally NFA was replaced by CS and PGBS, was shifted to gauge the flowability of CS and PGBS incorporated mortars. The mortar was filled in three layers for the oil mould and was placed on the table. The flow table with mortar was jolted 25 times after vertically removing the mould. The diameter of the spread of mortar was measured in four directions to calculate the average spread, which gave the fluidity of mortar to the spread diameter.

Graphs were plotted based on the spread diameter versus % of SP/C to determine the ideal dosage of SP. The saturation point was the dosage of SP beyond which spread diameter will not increase on further addition of SP but will result in segregation. A graph was plotted for the flow percentage versus dosages of SP. The curves at the dosage value beyond which the super-plasticizer would not build the flow with an increment in a dosage of SP and the flow is resolved.

3.3.1.3 Mix proportion of concrete

The mix proportion of concrete was prepared for M40 grade concrete, according to IS: 10262-2009 and IS:456-2000. Concrete mixtures having a w/c of 0.35 and SP dosage of 0.6% were adopted. The mix proportions are mentioned in Table 3.12. Concrete cubes and cylinders were prepared, cured, and then tested at the age of 7, 28, 56, 90, 180, 270, and 365 days. The average of three values was recorded as the strength of concrete. Further, 365 days cured sample was used for SEM analysis.

Table 3.12 Mix proportion of concrete

Cement (kg/m^3)	**Fine Aggregate (kg/m^3)**	**Coarse Aggregate (kg/m^3)**	**Water (kg/m^3)**	**Superplasticizer (kg/m^3)**
410.51	650	1268.62	143.68	2.46

3.3.1.4 Slump test

Recent advancements revealed that researches had been carried out for industrial waste materials to achieve maximum workability using the slump test in concrete. Various rages suggested ranges for by IS: 456 - 2000, and for this research work, medium workability was adopted.

According to the method mentioned in IS: 1199 - 2004, the procedure was followed using a slump cone of dimension specified in IS: 7320 - 2004 to measure the workability by using slump test on concrete mixtures at the saturation dosages (as obtained in flow table test). In this study, the fresh concrete was placed in four layers in a slump cone, providing sufficient tamping to each layer. Measurement of slump value was carried out on the removal of mould as the concrete started to subsidence.

3.3.1.5 Curing regime

Figure 3.5 shows the curing of concrete specimens in freshwater. To compare the behaviour of concrete based on natural curing conditions, the same combination of each set of specimens was exposed to tap water (FW) curing and seawater (SW) curing respectively. All combinations of concrete specimens were cured by immersing in tap water in the curing tank. The various combinations of concrete exposed to fresh water and seawater curing conditions are shown in Table 3.13.

In the case of seawater curing, the specimens were shifted to the nearby shore. Figure. 3.6 shows the process adopted in placing the concrete cubes inside the seawater. The specimens cured in the sea were exposed to all-natural changes that happen in the sea of the tidal zone and periodic measurement of salinity, dissolved oxygen and pH of sea water was recorded. However, the depth of the place where concrete specimens was exposed was not measured as the bags were tied to the rocks present in the tidal zones. Galvanized wire bags of heavy gauge, which were available in the form of mats with the gaps in between were designed to bear the load of the specimens by the local manufacturers. The bags with the specimens were shifted to the sea for exposure in the tidal zone. The combinations of concrete was prepared by replacing NFA using CS and PGBS separately for the different types of exposure conditions.

Figure. 3.5 Curing of concrete specimens in freshwater

Table 3.13 Combinations of concrete exposed to fresh water and seawater curing conditions

Replacement of NFA by CS cured in freshwater (CS FW)	Replacement of NFA by CS cured in sea water (CS SW)	Replacement of NFA by PGBS cured in fresh water (PGBS FW)	Replacement of NFA by PGBS cured in sea water (PGBS SW)
CS FW 0%	CS SW 0%	PGBS FW 0%	PGBS SW 0%
CS FW 10%	CS SW 10%	PGBS FW 10%	PGBS SW 10%
CS FW 20%	CS SW 20%	PGBS FW 20%	PGBS SW 20%
CS FW 30%	CS SW 30%	PGBS FW 30%	PGBS SW 30%
CS FW 40%	CS SW 40%	PGBS FW 40%	PGBS SW 40%
CS FW 50%	CS SW 50%	PGBS FW 50%	PGBS SW 50%

	
(a)	**(b)**
	
(c)	**(d)**
	
(e)	**(f)**

(g)

(h) (i)

Figure. 3.6. Process of placing the concrete cubes into the sea

(a) Preparation of bags; (b) Transferring of specimens to seashore; (c) Arrangement of cubes before placing in the sea; (d) Anchoring fishing buoy to the bags; (e) Bags before placing into sea; (f) Driving the bags from the seashore; (g) Before tying the bags to the rocks in the sea; (h) Removal of bags; (i) Specimens after exposed to seawater curing;

3.3.1.6 Compressive strength of concrete

(a) **(b)**

Figure. 3.7 Compressive strength test (a) Concrete specimens after removing from the seawater (b) Compressive testing machine

Figure 3.7 (a, b) shows the compressive strength test of concrete cubes. The compressive strength test provides an idea about all the characteristics of concrete which demonstrates the ability of the material or structure to carry the loads on its surface without any crack or deflection. Test for compressive strength is carried out as per the standard test method of ASTM C39/C39M similar to IS: 516 -1959 (Re 2004). The following combinations of concrete cubes of mix M40 of size 150×150×150 mm were cast for experiment and tested for compressive strength.

3.3.1.7 Splitting tensile strength of concrete

Figure. 3.8 Splitting tensile strength of the concrete

Figure 3.8 shows the splitting tensile strength of the concrete. The tensile strength of concrete greatly affects the size of cracking in structures. So, it becomes necessary to determine the tensile strength of concrete to determine the load at which the concrete members may crack. The procedure based on ASTMC 496, which is similar to IS:5876 - 1999, is followed in this work. Cylinders of size 300 mm height and 150 mm diameter were prepared, confirming to IS:10086 -1982.

3.3.2 Durability studies of concrete

An identifiable, unwanted condition which is not a part of the original intent of design of concrete structures is termed as deterioration of concrete, currently has become an earnest topic of importance for researchers. The aggressive effects on concrete endures are dynamic subject to new investigations, and few imperative facts have already been cited. Concrete has always proved an outstanding structural and durability performance but is most affected to early disintegration when exposed to the marine environment. Recent advancement in the concrete technology has revolutionized the mixture of various conventional ingredients to uplift the desired properties of concrete which have renewed its definition

3.3.2.1 *Leaching of concrete specimen using toxicity characteristic leaching procedure (TCLP) method.*

Figure 3.9 shows the leaching of concrete specimens used to determine the durability properties of concrete using toxicity characteristic leaching procedure (TCLP) method. Method 1311was adopted for leaching procedure.

Figure. 3.9 Leaching of concrete specimen

1. Solid to liquid ratio of 1: 10 is prepared as per standard leaching procedure.
2. 25g of fine concrete powder containing different partial replacements of NFA by CS and PGBS concrete powder (particle size - 90micron sieve) is mixed with 250 ml of distilled water and stirred well for 8 hours using a magnetic stirrer.
3. The particles in the solution are allowed to settle for 5 min and then subjected to a pressure filter. The filtered solution collected in the pressure filter flask is transferred to a conical flask.

3.3.2.2 Determination of pH Value in concrete

Figure. 3.10 pH of concrete

Figure 3.10 shows the determination of the pH value of concrete using pH meter. pH is a term used universally to express the intensity of a solution's acid or alkaline condition. The concentration of both Hydrogen and Hydroxyl ions in pure water is 10^{-7} moles/L. Hence the pH of neutral water is equal to: $\text{Log}_{10}[1/H^{+}] = \log_{10}[1/10^{-7}] = \log_{10} 10^{7} = 7$. Changes in pH will cause dissociation of ions and hence will influence the chemical reactions. pH can be measured electrometrically or colorimetrically.

Procedure

1. Rinse the electrode with distilled water (D.W) and dry it using tissue paper.
2. Immerse the electrode in a suitable buffer solution, say 7.00 pH (nearest to the range to be measured). Make the necessary corrections for temperature etc.
3. Measure the pH. Adjust the calibration knob to bring the reading to the correct value.
4. Rinse the electrode with D.W. and Dry it using tissue paper. Place the electrode in the concrete leached sample whose pH is to be measured and note the reading.

3.3.2.3 Determination of electrical conductivity in concrete

EC of water is directly proportional to the dissolved minerals in the water. The unit of EC is microohms/cm or microsiemens/cm. (reciprocal of resistance) EC varies directly with temperature and is generally reported at 25^0C.

Procedure

1. Take a concrete leached solution.
2. Clean the electrode with D.W. and dry it. Dip it in the solution.
3. Adjust the temperature compensation dial to 250C (or 0.0191 C^{-1}) / or temperature knob to solution temperature.
4. Rinse the electrode with D.W., dry it and immerse it in the sample.
5. Read the conductivity and note the temperature.

3.3.2.4 Determination of dissolved oxygen (D.O.) for curing water

It is necessary to know the D.O. level to assess the quality of raw water and check stream pollution. A minimum D.O. of 4 to 5 mg/l is desirable for the survival of aquatic life. Higher values of D.O. may cause corrosion of Iron and steel.

In this Winkler's modified analysis method, the oxygen present in the water sample oxidizes the divalent manganous ion to its higher valency, which precipitates as a brown hydrated oxide after the addition of sodium hydroxide (NaOH) and potassium iodide (KI). Upon acidification, manganese reverts to a divalent state and liberates iodine from KI equivalent to D.O. content in the sample. The liberated iodine is titrated against sodium- thiosulphate (0.025N), using freshly prepared 2% starch solution as an indicator. If the oxygen is absent in the sample, the manganese sulphate ($MnSO_{4)}$ reacts with the alkali to form white precipitate manganese hydroxide (Mn $(OH)_2)$.

a) Reagents

- **Manganous sulphate solution**

  Dissolve 480g $MnSO_44H_2O$ or 400g $MnSO_4$ $2H_2O$ or 364 g $MnSO_4H_2O$ in D.W., filter, and dilute to 1L. The solution should not give colour with starch when added to an acidified KI solution.

- **Alkali iodide-azide reagent**

  Dissolve 500 g NaOH or 700 g KOH, 135 g NaI or 150 g KI in D.W. and dilute to 1l. Dissolve 10 g Sodium Azide, NaN_3 in 40 mL D.W. and add this to the reagent prepared. This solution, when diluted and acidified should not give colour with starch.

- **Standard Sodium thiosulphate solution, 0.025N $Na_2S_2O_3.5H_2O$**

  Dissolve 6.205g $Na_2S_2O_3.5H_2O$ in freshly boiled D.W. Add 1.5mL 6N NaOH solution or 0.4g solid NaOH and dilute it up to 1L.

- **Standard Potassium dichromate, $K_2Cr_2O_7$ Solution, 0.025 N**

  Dissolve 1.226g anhydrous Potassium dichromate, $K_2Cr_2O_7$ in D.W. and dilute to 1000 mL

- **Hydrochloric acid, 2N HCl**

  Add 166 ml of concentrated Hydrochloric acid to D.W., mix it and dilute to 1L.

- **Concentrated Sulfuric acid, H_2SO_4**

- **Potassium iodide powder**

- **The freshly prepared Starch solution, 2%**

  Make a paste of 5 g Starch with a little cold D.W., add to 250 mL boiling D.W., stir it and allow overnight to settle. Use a clear supernatant solution.

(b) Procedure

Standardization of Sodium thiosulfate solution

Standardize the sodium thiosulfate solution using a 0.025 N $K_2Cr_2O_7$ solution. Take 10 ml of $K_2Cr_2O_7$ solution in a conical flask. Add 2 ml of 2N hydrochloric acid solution and one spatula of potassium iodide (KI) powder. The solution turns brown. Titrate against Sodium thiosulphate solution till color turns to pale yellow. Add 0.5 to 1 ml starch solution. The colour turns blue. Continue the titration till the blue becomes colorless. Calculate the Normality of Sodium thiosulphate.

Collect the sample in the B.O.D. bottle up to the neck, taking care to avoid any air bubbles while collecting. To this, add 1 ml $MnSO_4$ solution followed by 1 ml alkali – iodide – azide solution, holding pipette tips just above the liquid surface. Stopper the bottle carefully to exclude the air bubble and mix it by inverting it 25 to 30 times. Allow the precipitate to settle down to leave a clear supernate above manganese hydroxide floc.

Add 1 to 2 ml concentrated sulfuric acid, restopper and mix immediately by inverting the bottle till all the precipitate dissolve. Titrate 201 ml sample against 0.025N $Na_2S_2O_3$ till pale yellow colour is obtained. Add 1 ml starch; continue titration till the dark blue becomes colorless. The amount of dissolved oxygen is calculated as per Equation (3.1) as per IS 10500 : 2016.

Calculation

For 200 mL of sample taken, 1 ml of 0.025 N $Na_2S_2O_3$ = 1 mg O_2 / L

$$\text{Dissolved oxygen as mg/L} = \frac{N\ Na_2S_2O_3 \times V\ Na_2S_2O_3 \times 8000}{\text{Volume of sample}} \qquad (3.1)$$

3.3.2.5 Determination of alkalinity for curing water

Alkalinity is the presence of sufficient alkaline ions in water. The determination of alkalinity is very useful in water and wastewater because it provides buffering to resist changes in pH value. Alkalinity is due to the presence of bicarbonate and carbonate or hydroxide ions in water. This is usually expressed as Total alkalinity and Caustic alkalinity (i.e. when the pH is above 8.3).

Alkalinity is measured titrimetrically by titrating against Dilute Sulphuric acid. Phenolphthalein and methyl orange are used as indicators to indicate pH 8.3 and pH 4.3. The phenolphthalein produces a pink colour when the pH is above 8.3 and colourless when pH is below 8.3. Methyl orange is slightly orange when the pH is above 4.3 and becomes wine red when pH is below 4.3. The amount of acid consumed to reach the phenolphthalein endpoint is used to calculate the phenolphthalein (P) alkalinity. The total acid consumed to reach pH 4.3 is used to calculate the total (T) alkalinity. From the values of ‘P’ and ‘T’, the species of alkalinity can be determined.

3.3.2.6 Determination of chloride concentration in concrete

Chlorides in natural waters can be attributed to leaching of chloride-containing rock and soils, discharges of effluents from chemical industries, sewage disposal, irrigation drainage, seawater intrusion in coastal regions. Chlorides, associated with sodium exert a salty taste, when their concentration is more than 250 mg/l. Excess chlorides can also corrode concrete by extracting calcium in the form of calcite. Chloride ion is determined by Mohr's method, titration with standard silver nitrate solution in which silver chloride is precipitated at first. The end of titration is indicated by the formation of red silver chromate from excess $AgNO_3$ and potassium chromate used as an indicator in neutral to a slightly alkaline solution.

(a) Reagents

- **Standard sodium chloride solution, 0.0141N**

  Dissolve 824.0 mg NaCl (Dried at 140^0 C) and dilute to 1000 mL; 1 mL = 500 µg Cl^-

- **Standard Silver nitrate solution, 0.0141N**

  Dissolve 2.395 g $AgNO_3$ in D.W. and dilute to 1000 mL

- **Potassium chromate indicator solution**

  Dissolve 50 g K_2CrO_4 in little D.W. Add $AgNO_3$ solution till a definite red precipitate is formed. Let stand 12 h, filter, and dilute to 1 l with D.W.

(b) Procedure

Standardization of Silver Nitrate Solution

Titrate 10 ml of 0.0141N Standard sodium chloride solution against $AgNO_3$ solution. Use ten drops of potassium chromate solution as an indicator. The colour change is from yellow to pinkish yellow. Be consistent in endpoint recognition. Titrate 10 ml of distilled water using ten drops of potassium chromate indicator solution. The endpoint is the same as above. A blank of 0.2 or 0.3 ml is usual.

Sample Titration

Titrate 1 ml of the leached sample directly using the same quantity of indicator and titrate it against standard $AgNO_3$ solution till the endpoint is obtained when the colour changes from yellow to brick red. The equation (3.2) is used to determine the concentration of chloride in concrete.

$$\text{Chloride (mg/l as Cl}^{-}\text{)} = \frac{(A - B) \times N \times 35460}{V} \qquad (3.2)$$

A = titration for sample (ml)

B = ml titration for Blank

V = ml of sample taken

3.3.2.7 Determination of sulphate concentration in concrete using spectrophotometer test

Sulphates occur naturally in water as a result of leaching from gypsum and other common minerals. Contaminated waters and wastewater usually have high sulphate concentrations. Barium Chloride reacts with the sulphate in water to form barium sulphate, which settles after some time. In this work, a spectrophotometer test is adopted to determine the concentration of sulphate in concrete.

(a) Reagents

- **Buffer solution**

  Dissolve 30 g Magnesium chloride, $MgCl_2\ 6H_2O$, 5 g Sodium acetate, $CH_3COONa.3H_2O$, 1 g Potassium nitrate, KNO_3 and 20 ml Acetic acid,

CH_3COOH (99%) in 500 ml D.W. and dilute to 1 l. (For samples having sulphate concentration less than 10 mg / l, add 0.111g Sodium sulphate, Na_2SO_4 to the 1l buffer solution and use.

- **Barium chloride, $BaCl_2$, crystals**
- **Standard sulphate solution**

Use of any one method gives standard sulfate solution of concentration 100 mg / l (1 ml = 100 µg SO_4^{2-})

Dilute 10.4 ml of Standard 0.0200N sulfuric acid solution to 100 ml

Dissolve 0.1479 g anhydrous Na_2SO_4 in D.W. and dilute to 1000 ml

(b) Procedure

Spectrophotometer test for standard solution

Preparation of Standard Solution

Prepare standards at 5 mg / l increments in the range of 0 to 40 mg/l by accurately pipetting the calculated volume of standard sulphate solution, diluting it to 100 mL, and transfer into conical flasks. To this, add 20 ml of buffer solution and the whole solution is placed on the magnetic stirrer and subjected to stir at a constant speed. Then add a spatula of barium chloride crystals and stir for 60 ± 5 seconds. The solution is allowed to rest for five minutes after which the colorimeter reading is taken for absorption or percentage transmission at 420 nm. Plot the graph taking concentration along X-axis and abs / % along Y-axis.

Sample Preparation

100 ml of sample is taken in a conical flask, and to this 20 ml of buffer solution is added and mixed in a magnetic stirrer at a constant speed. One spatula of barium chloride is added to the solution and combined with a stirrer for 60 ± 5 seconds at a constant rate. Allow reaction time of five minutes, then take reading for absorption/percentage transmissibility. Express the sulphate concentration of the given water sample as mg SO_4^{2-} /l.

Graph

Absorbance values of different samples will be plotted along the Y-axis for the standard graph line graph. Drop a perpendicular (parallel to the Y-axis) from the point where the absorbance values intersect the standard graph line to determine the percentage of concentration of sulphates absorbed by concrete along the X-axis.

3.3.2.8 Determination of sodium concentration in concrete using flame photometry test

Both the standard stock solution and sample solution are prepared in fresh distilled water. The flame of the photometer is calibrated by adjusting the air and gas. Then the flame is allowed to stabilize for about 5 min. The leached solution was subjected to the test and the readings of the galvanometer are recorded to find out the concentration of the element in the sample.

3.3.2.9 Determination of salinity in sea water

Salt refractometers are used to measure sodium chloride dissolved in water. Seawater refractometers are used to measure the mixture of salts typically found in seawater.

Procedure

Open the plate near the angled end of the refractometer: A handheld refractometers have one round, open end to look through and one angled end. Hold the refractometers, so the angled surface is on the top of the device, and find the small plate near the end which can be moved to one side. Add a couple of drops of the liquid onto the exposed prism: Take the liquid to measure and use an eyedropper to pick up a couple of drops of it. Transfer this to the translucent prism revealed when moved the plate. Add enough water to cover the prism's surface with a thin layer completely.

Close the plate carefully: Cover the prism again by gently pushing the plate back into position. The parts on a refractometer may be small and delicate, so try not to apply much force even if they become slightly stuck. Instead, wiggle the plate back and forth with a finger until it moves smoothly. Look through the device to see the salinity reading: Look through the round end of the device. There should be one or more numbered scales visible. The salinity scale is likely labeled 0/00, meaning “parts per thousand", and ranges from 0 at the bottom of the scale to at least 50 at the top. Look for the salinity measurement at the line where the white and blue areas meet. The monthly variation of temperature, salinity, dissolved oxygen, and pH of the seawater measured during the research work are represented in Table 3.14.

Table 3.14 Seawater Analysis

Sl. No	Month	Temperature (˚C)	Salinity (ppt)	Dissolved Oxygen	pH
1	Jan	29.5	34	4.1	8.2
2	Feb	32.0	35.2	3.6	8.03
3	Mar	33.0	38.7	3.4	8.0
4	Apr	33.0	35.5	4.0	7.94
5	May	32.0	35.1	4.8	7.85
6	Jun	27.5	33	3.2	7.5
7	Jul	28.0	32.6	5.6	7.4
8	Aug	27.5	29.8	4.0	7.5
9	Sept	29.0	31.3	4.0	7.8
10	Oct	31.5	31.5	3.5	8.0
11	Nov	30.0	35.4	4.5	7.9
12	Dec	29.0	34.1	4.1	8.1

3.4 MICROSTRUCTURE STUDY OF CONCRETE

The microstructure study was carried out for the concrete cured in fresh water and sea for 365 days using Scanning Electron Microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDS) analysis. This study helps to examine the microstructure, thereby analyzing the material.

3.4.1 Scanning Electron Microscope and Energy-dispersive X-ray spectroscopy analysis

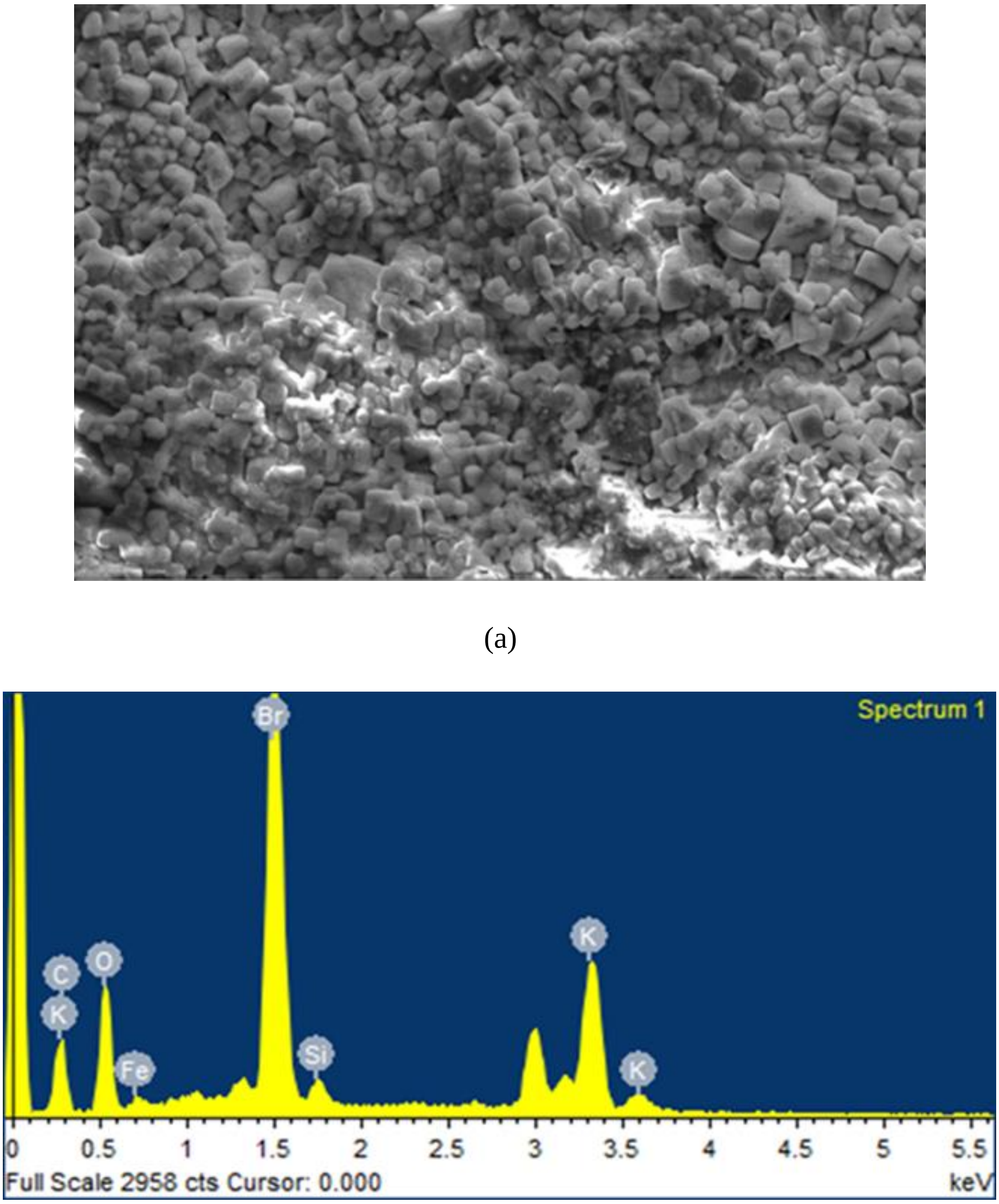
SEM is one of the best methods for studying the morphology of hydration products. There are various methods followed for the sample preparation, and generally thin sections or surface of the fractured specimen are used for the analysis. After conducting the compressive strength on the cube specimens, a sample size 2-4 mm was extracted from the crushed cubes for SEM studies. The specimens were then placed onto the studs using adhesive tapes. The studs along with the specimens exposed to gold plating for 90 seconds. Then the stud is loaded onto the Scanning Electron Microscope for further scanning. Second, secondary electron (SE) imaging of fracture surfaces is a somewhat easier approach that yields direct images of the microstructure. The elemental composition of CS is obtained by Energy-dispersive X-ray spectroscopy (EDS) analysis.

3.4.2 SEM and EDS images analysis of copper slag aggregate

The SEM micrograph revealed that CS particles are black in colour with a glassy texture and irregular shape. Morphologically, CS particles were studied by scanning electron microscopy (SEM) and, as seen in the Figure. 3.11a, showed irregularly sized grains, with smooth and very low porosity surfaces, possibly describing its low water absorption. The elemental composition of CS was obtained by Energy-dispersive X-ray spectroscopy (EDS) analysis as shown in Figure. 3.21b. The primary element present were found to be iron, oxygen, silicon, and carbon. Microscopic observations showed a maximum of the CS grains are well crystallized. Also, it includes iron oxides, other oxides such as silica, alumina, lime, and magnesia that constitute 95% or more of the total oxides.

3.4.3 SEM and EDS images analysis of PGBS aggregate

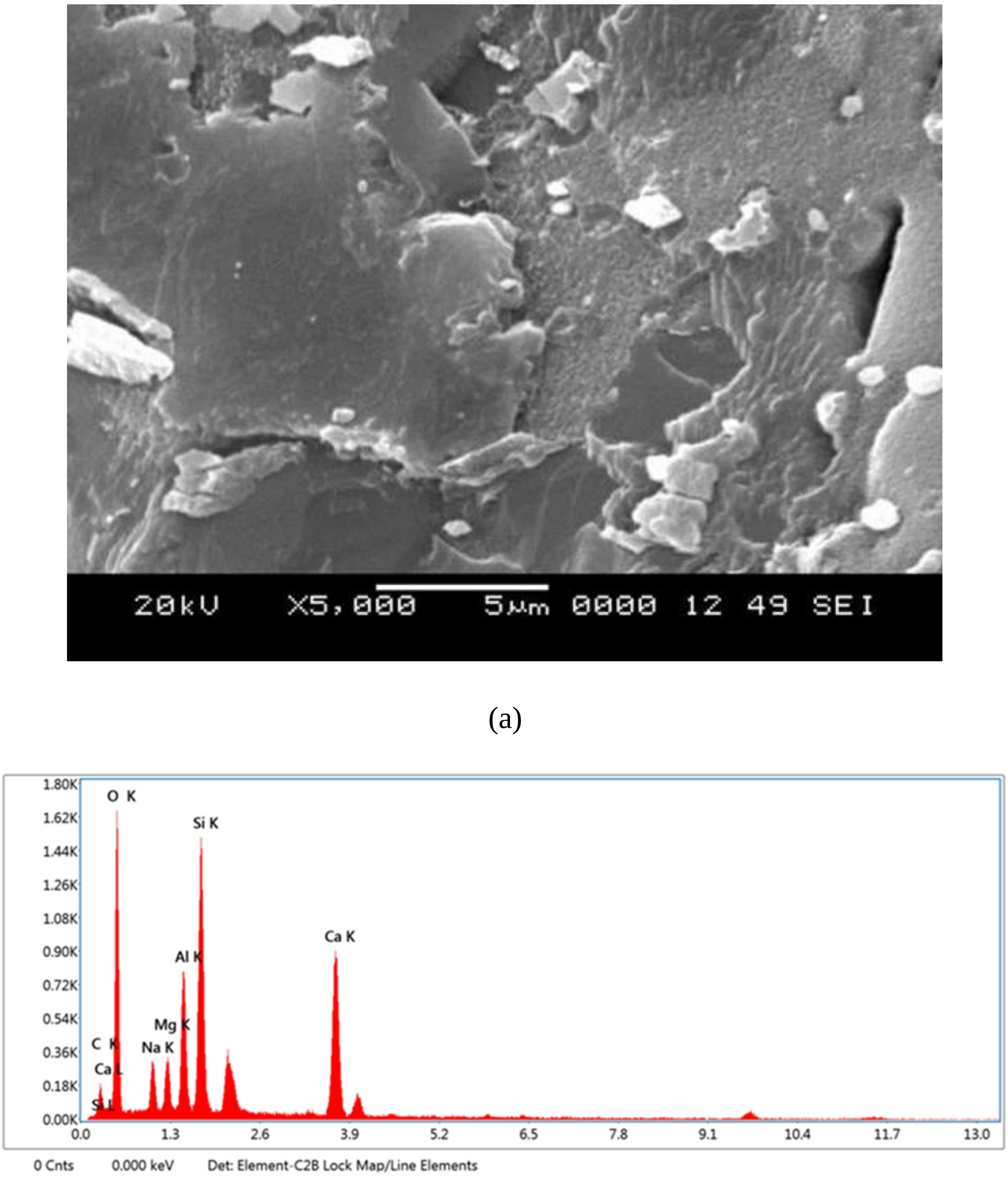
The SEM and EDS images of PGBS aggregate is shown in Figure 3.12 (a, b). Inequigranular grey to buff coloured loose sandy material with fine angular grains of varying sizes and colour. Iron oxide was also observed. It is composed of angular fragments of silica glass, quartz, altered feldspar, and iron oxide. Silica glass was the dominant grain present. Silica glass is a colourless angular to subangular in shape with varying sizes without cleavages. It showed curved fractures/cracks at places. Iron oxide strains are also noticed at places. On the prime facie, the sample was silica glass rich sand and appears suitable for use as NFA in construction works.



(a)

(b)

Figure. 3.11 Microstructure study of CS aggregate (a) SEM image of CS aggregate (b) EDS image of CS aggregate



(a)

(b)

Figure. 3.12 Microstructure study of PGBS aggregate (a) SEM image of PGBS aggregate (b) EDS image of PGBS aggregate

3.5 CLOSURE

The materials used to prepare the concrete play a vital role in the design mix of the concrete as the properties of every material decide the strength and durability characteristics of concrete. Accordingly, the choice of materials used in this research work was based on many factors like manufacturing of the material, availability, affordability, transportation, maintenance and socio economic and environment friendly. In order to evaluate the characteristics of concrete related to its quality and performance in both fresh and hardened state, the concrete prepared for marine environment application had undergo many tests to determine the concrete serviceability.

CHAPTER 4

RESULTS AND DISCUSSION

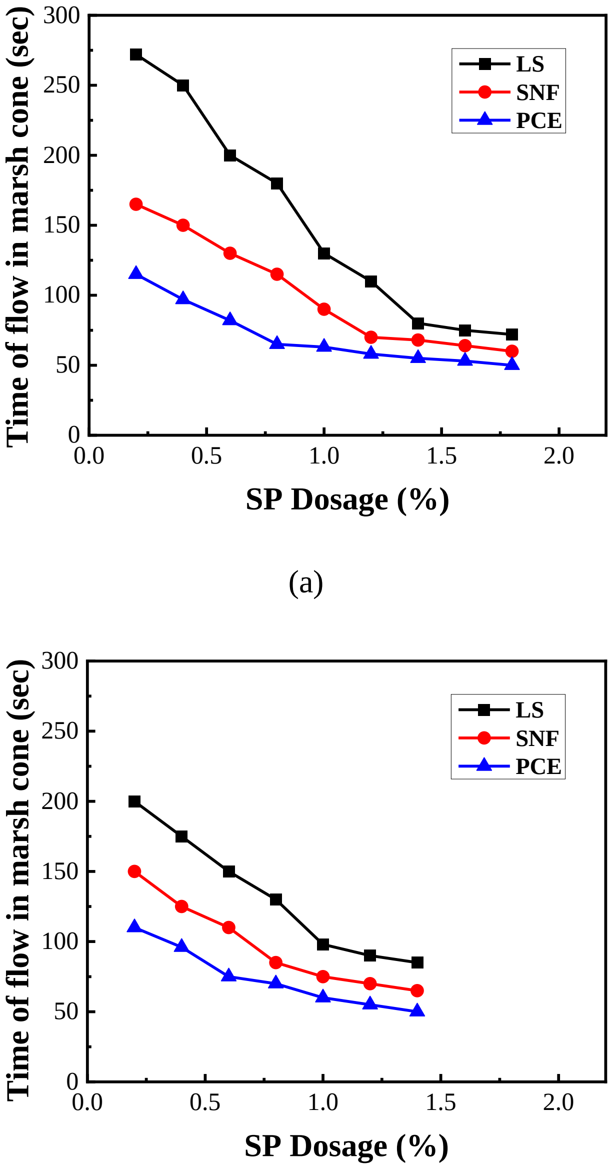
4.1 FRESH AND HARDENED PROPERTIES OF CEMENT PASTE, MORTARS, AND CONCRETE.

The properties of materials were determined in both fresh and hardened state. The behaviour of concrete varies

4.1.1 Marsh cone test

The behaviour of cement with different types and dosages of SP to determine optimum dosage was carried out using marsh cone test. The results of the marsh cone test for OPC aand PPC are shown in the Figure 4.1 (a,b). Accordingly, the optimum dosage obtained for PCE based SP are 0.7% for OPC and 0.6% for PPC. For SNF based SP the optimum dosages obtained are 0.85% for OPC and 0.8% for PPC. Similarly, for LS based SP the optimum dosage obtained for OPC and PPC are 0.9% and 0.85%.

To achieve the steeper decline in w/c, enhancing the workability of the control mix of concrete for OPC mixes, can be modified and controlled using SP despite unpredictable conditions based on the compatibility between the choice of SP and type of cement. Flow time decreases with an increase in the dosage of SP, and the optimum dosage varies with different types of SP. In the case of blended cement like PPC, the fineness of fly ash particles and its spherical shape enhanced the fluidity of the cement paste by reducing the porous compared to non-blended cement improved the rheological properties with the lower dose of SP.



(a)

(b)

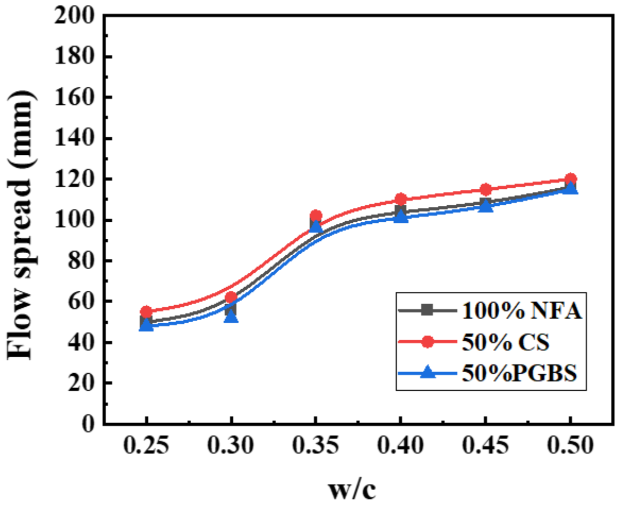
Figure 4.1 Marsh cone test (a) OPC Mix (b)PPC mix

4.1.2 Flow table test

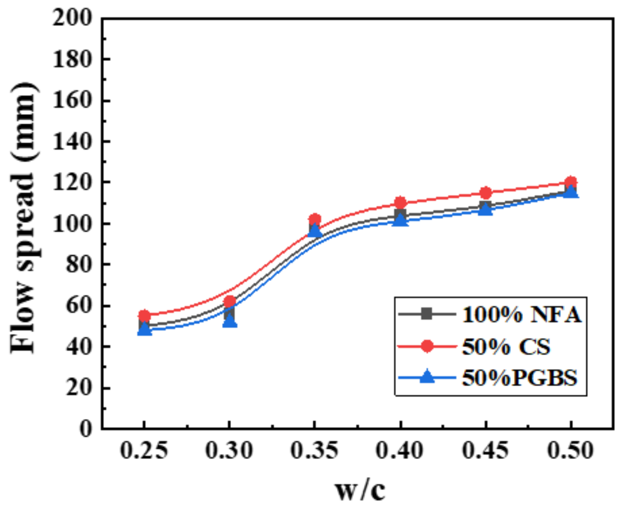
Based on the results obtained from the marsh cone test, it was noted that PCE based SP would provide better flow when compared to other types of SP used in the tests. Therefore, PCE based SP was considered to carry out the flow table test of mortars. The difference in the water absorption of NFA, CS, and PGBS will show variation in the flow of mortars. As a result, it becomes important to determine the optimum dosage of SP and w/c required to achieve the better flow. Accordingly, the variation in the flow of mortars was noted.

4.1.2.1 Behaviour of flow of mortar for OPC and PPC mixes with partial replacement of CS and PGBS to determine w/c without using SP

Figure 4.2 (a,b) represents the flow of mortar mixes without SP. The optimum w/c for OPC and PPC control mixes without SP obtained was 0.47% and 0.43% respectively, for the mix having 100% NFA. The w/c for OPC and PPC mixes for 50% replacement of NFA by CS obtained was 0.42% and 0.4% respectively, as water absorption of CS is less when compared to other mixes. The w/c for OPC and PPC mixes for 50% replacement of NFA by PGBS obtained was 0.5% and 0.45% respectively. The flow has decreased with the increase in the percentage replacement level of NFA by PGBS. This is because of the difference in the water absorption of the aggregates irrespective of variation in w/c. For the mix with w/c 0.35, the mix appeared harsh with the presence of less water on the surface of the mortar. The flow has tried to increase with the increase in w/c. For 100% NFA mortars typical behaviour of PPC showed slightly higher flow without indication of bleed when compared to OPC mixes. In the case of 50% CS mortars, the behaviour was similar to no replacement, but in 50% PGBS, mortar mixes demanded higher water.



(a)



(b)

Figure 4.2 Flow of mortar without SP (a) OPC Mix (b)PPC mix

4.1.2.2 Behaviour of flow of mortar with partial replacement of CS and PGBS using SP for various w/c.

The flow of mortars was determined by partially replacing NFA using CS and PGBS aggregates for different w/c and various dosages of SP. Since water absorption of aggregates varies, this helps to determine the optimum w/c and dosage of SP to achieve the desired flow.

Figure. 4.3 (a, b) represent the mortar mix flow by partially replacing CS and PGBS for NFA for w/c 0.4. The flow increased with the addition of SP. The behaviour of flow in PPC was smoother, probably better particle distribution The optimum dosage obtained for OPC and PPC mixes for 100% replacement by NFA showed a slight variation. The flow characteristics were better for 50% replacement of NFA by CS. The maximum difference in spread of the flow was 3 - 4 mm based on variation of SP dosage was noted when compared to other mixes. In the case of 50% replacement of NFA by PGBS, the mix appeared to be stiff at the initial level, but significant improvement in the flow of mortars was observed with the increase in dosage of SP.

In the case of PPC mortar mixes, the mix appeared to be more cohesive, and the spread of the mortar increased with an increase in dosage of SP. The mix without SP showed a difference of 5 mm between 100% and 50% PGBS replaced mix. The flow started to decrease with the increase in the replacement level of NFA. However, the better spread of the mortar mixes has been achieved for the minimum w/c providing better workability.

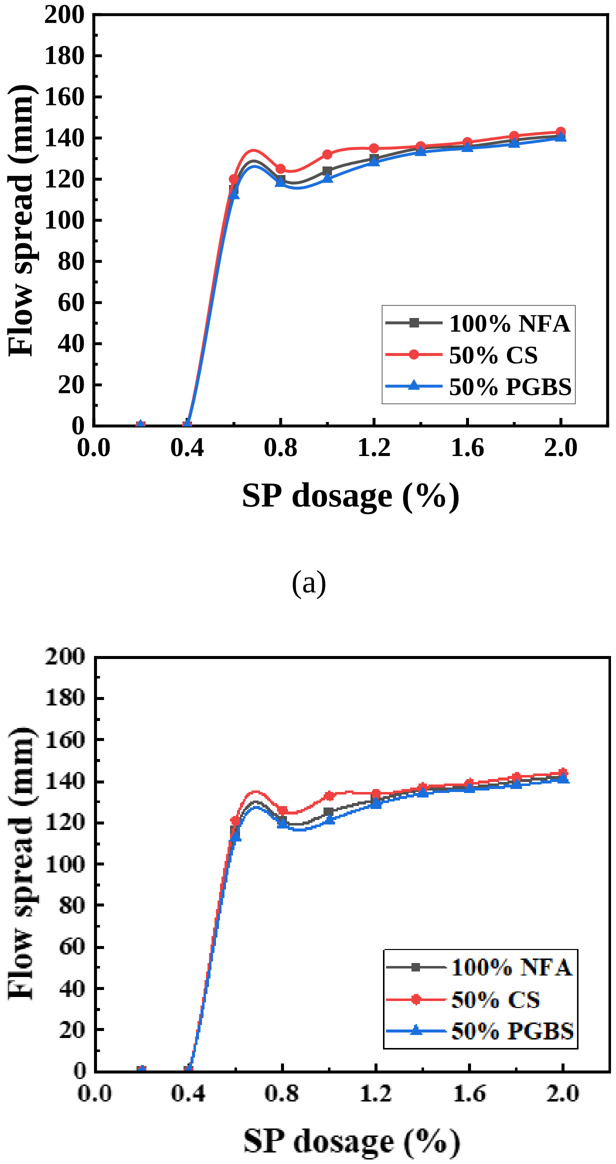
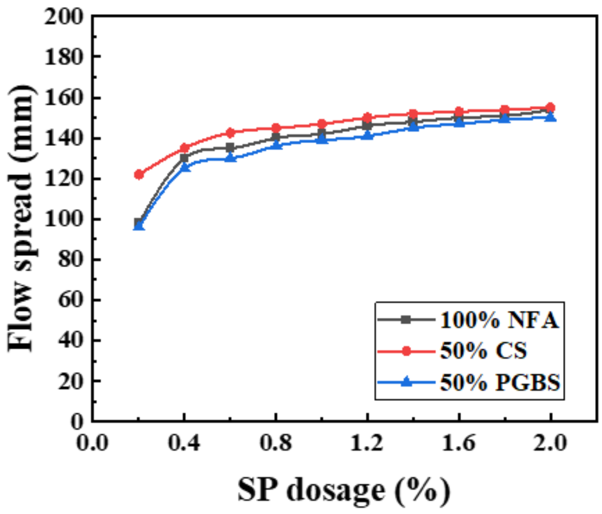


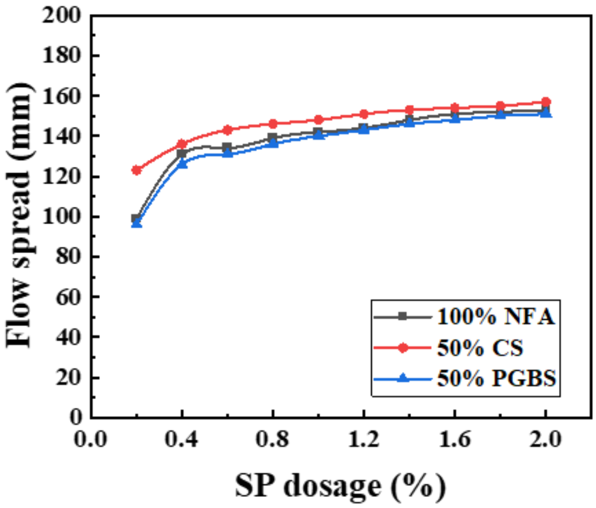
Figure 4.3 Flow of CS and PGBS mortar for 0.4 w/c (a) OPC Mix (b)PPC mix.

From the Figure. 4.4 (a, b), the optimum dosages obtained for OPC mixes is 0.7%. The flow appeared to be smooth, and the mix was cohesive. The same mix, when replaced partially with 50% of NFA by CS, the spread of the mortars increased by 6mm. For very less dosage of SP, improvement in the flow of mortars was recorded. This might be due to an increase in the w/c from 0.4 to 0.45. However, the performance of all mortar mixes, including PGBS mortars, the workability appeared to be consistent. In the case of PPC mixes, the workability of mortars was observed was 0.65%. There was no significant variation in mortars' flow compared to OPC mixes having PCE-based SP. Mortars with 50% replaced NFA by CS achieved better flow when compared with mortars having only NFA and mortars having 50% PGBS.

The flow has revealed better quality in the case of the texture of the mix, and the additional spread of the mortar was noted without any appearance of segregation or bleeding irrespective of the replacement of PGBS for NFA. The mix without SP showed a difference of 5.2 mm between 100% and 50% PGBS replaced mix. The flow started to decrease with the increase in the replacement level of NFA. The required workability was achieved for 0.6 % dosage of SP up to 30% replacement level for 0.45 w/c. The flow increased with the addition of SP. An increase in water indicated higher flow, but the observation of bleed started early for 50% CS mortar.



(a)

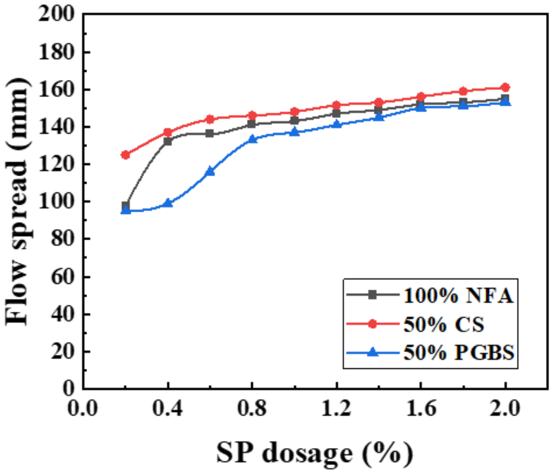


(b)

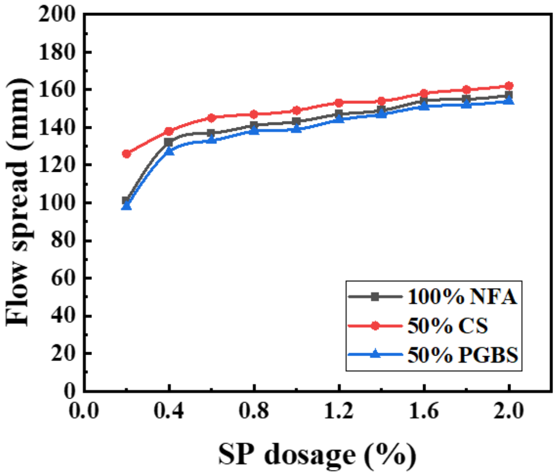
Figure 4.4 Flow of CS and PGBS mortar for 0.45 w/c (a) OPC Mix (b)PPC mix

Figure. 4.5 (a, b) represent the mortars flow for w/c of 0.5. The optimum dosages obtained for OPC and PPC mixes were 0.6% and 0.55% mix with only NFA. For 50% replaced NFA by CS the optimum dosage obtained were 0.55% and 0.5%. For partially replaced NFA by PGBS mix the optimum dosage obtained were 0.6% and 0.7%. The observation showed that there was a consistent increase in the spread of the mortars. An increase in w/c dropped down the percentage of SP dosage for all the mixes irrespective of the difference in water absorption of aggregates. Therefore, it becomes necessary to achieve a reliable flow with an optimum dosage of SP for optimum w/c, as the shape and size of the aggregates play a vital factor in mix proportion.

For the mixes with a w/c ratio of 0.5, the mortar flow value intensifies with water intake. The mix without SP showed a difference of 6 mm between 100% and 50% replaced mix. The small particle pore size of the PGBS slag absorbs water which results from more than water after the pores get filled though particle size is similar when linked with that of NFA, and the flow value increases. The rise in SP dosage prompts a decline in the yield stress, plastic viscosity, and an increase in mini-slump spread if the dosages are beneath the saturation point. Elsewhere the saturation dosage, these parameters are practically constant Jayasree and Gettu (2008). The flow of the mortar increases with the use of SP (Ramezanianpour et al. (1995) and Malagavelli and Paturu (2012)). Workability enhancement by the SP is mainly by an increase in the surface potential force, the solid-liquid affinity, and the steric hindrance mainly in PCE-based superplasticizer (Sathyan et al., 2018). The flow behaviour of mortar in the case of control mixes showed a better flow variation marginally when compared to PGBS mortars. This variation happens when the shape and surface features of the aggregate change along with water absorption of the aggregate replacement of NFA by C.S and PGBS for various dosage of SP respectively.



(a)



(b)

Figure 4.5 Flow of CS and PGBS mortar for 0.5 w/c (a) OPC Mix (b)PPC mix

4.2 CONCRETE SLUMP TEST

Figure 4.6 shows the slump test for combinations of concrete mixes. CS concrete mix showed better workability than PGBS concrete mixes with the increase in the replacement levels. It was observed that the shape and size of the aggregates, lesser water absorption, and other physical characteristics of CS aggregates had played a significant role in increasing the workability of the mix compared to the PGBS mix.

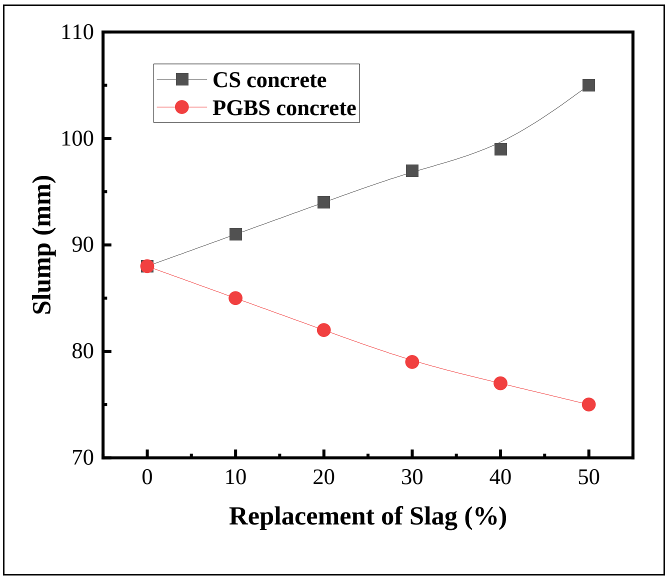
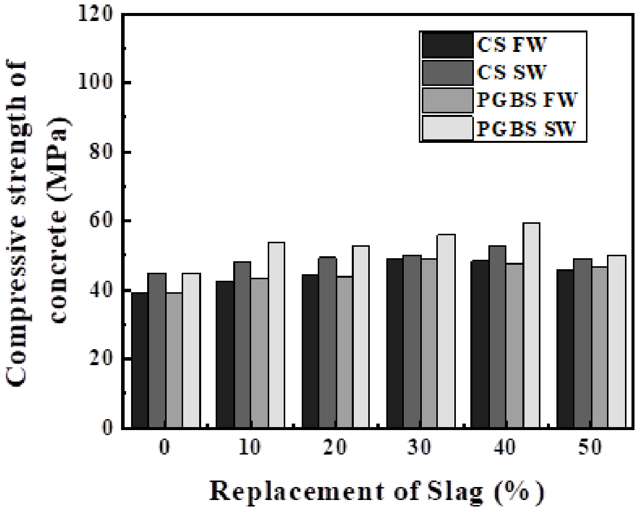


Figure 4.6 Workability of concrete

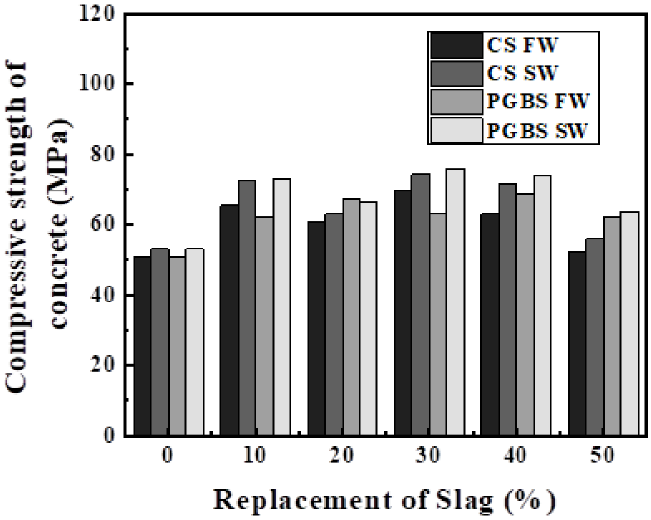
4.3 COMPRESSIVE STRENGTH OF CONCRETE

The compressive strength of the concrete specimens obtained at different ages when cured in fresh and seawater are shown in Figure. 4.7 (a to g). For all the concrete mixtures, the compressive strength obtained at relatively early ages (7 and 28 days) is higher than the seawater cured specimen compared to the specimens cured in freshwater. On the other hand, at the later ages (180 to 365 days), no significant strength difference is observed between the specimens cured in fresh and seawater. A similar trend is also observed for the split tensile strength shown in Figure. 4.8 (a to g). Both these results indicate the rate of strength development is faster at early ages when cured in seawater as compared to freshwater. However, the ultimate strength for concrete specimens remained the same irrespective of the curing regime. This can be explained based on the difference in temperature for the two curing regimes. The higher temperature enhances the rate of hydration at early ages resulting in a higher compressive strength at early ages. These results agree with a previous study by (Kumar et al., 1987) who observed the hydration of the four main anhydrous cement phases (C_3S, C_2S, C_3A, and C_4AF) accelerated at early ages when cured at higher temperatures. Another reason for the improved strength is that the seawater can promote the formation of Friedel's salt in concrete which accelerates the early age hydration (Escalante-Garcia et al.,1998).

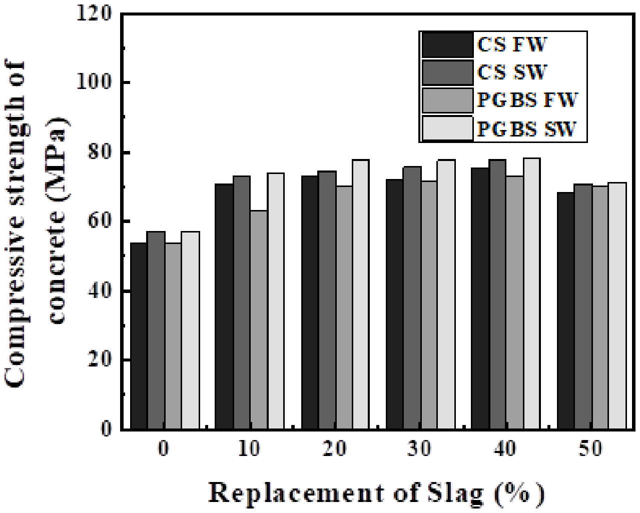
The free chlorides ions present in seawater can react with the Afm phase in hydrated cement paste from Friedel's salt, which refines the pore structure and enhances the early age strength (Ogirigbo et al., 2017, Shi et al., 2017). Another aspect that has to be examined is the influence of PGBS and CS replacement on the strength development of concrete. In the case of both CS and PGBS slag, at the age of 7 days, the addition of these slag aggregates did not significantly affect the compressive and the split tensile strength irrespective of the curing condition. However, for the strength values obtained at 28 to 365 days, an improvement in strength can be seen as NFA is replaced with CS and PGBS aggregates. In a previous study, Wu et al. (2010) studied the compressive strength development with various replacement levels of slag aggregates. They reported that the CS aggregates have better compressibility than NFA, which relieves the stress concentration and enhances the compressive strength of the concrete. Further, the angular shape of these aggregates provides a better interlocking with the cement matrix. The improvement in the strength may also be due to the modifications in the microstructure of the concrete due to the presence of the slag aggregates. For instance, Sharma et al. (2017) examined the microstructure of concrete containing different levels of CS aggregates. It was observed that in concrete mixtures containing CS aggregates, additional C-S-H gel is formed at the paste-aggregate interface, thereby reducing the interfacial transition zone (ITZ) thickness.


Compressive strength of concrete (MPa)
Replacement of Slag (%)
0
20
40
60
80
100
120
0
10
20
30
40
50
CS FW
CS SW
PGBS FW
PGBS SW

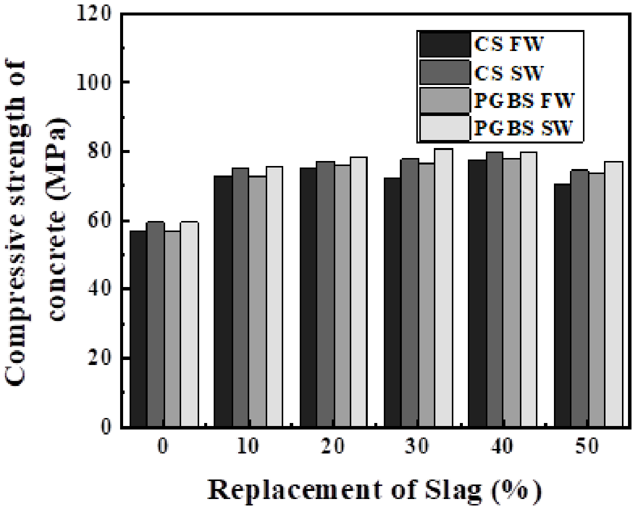
(a)


Compressive strength of concrete (MPa)
Replacement of Slag (%)
0
20
40
60
80
100
120
0
10
20
30
40
50
CS FW
CS SW
PGBS FW
PGBS SW

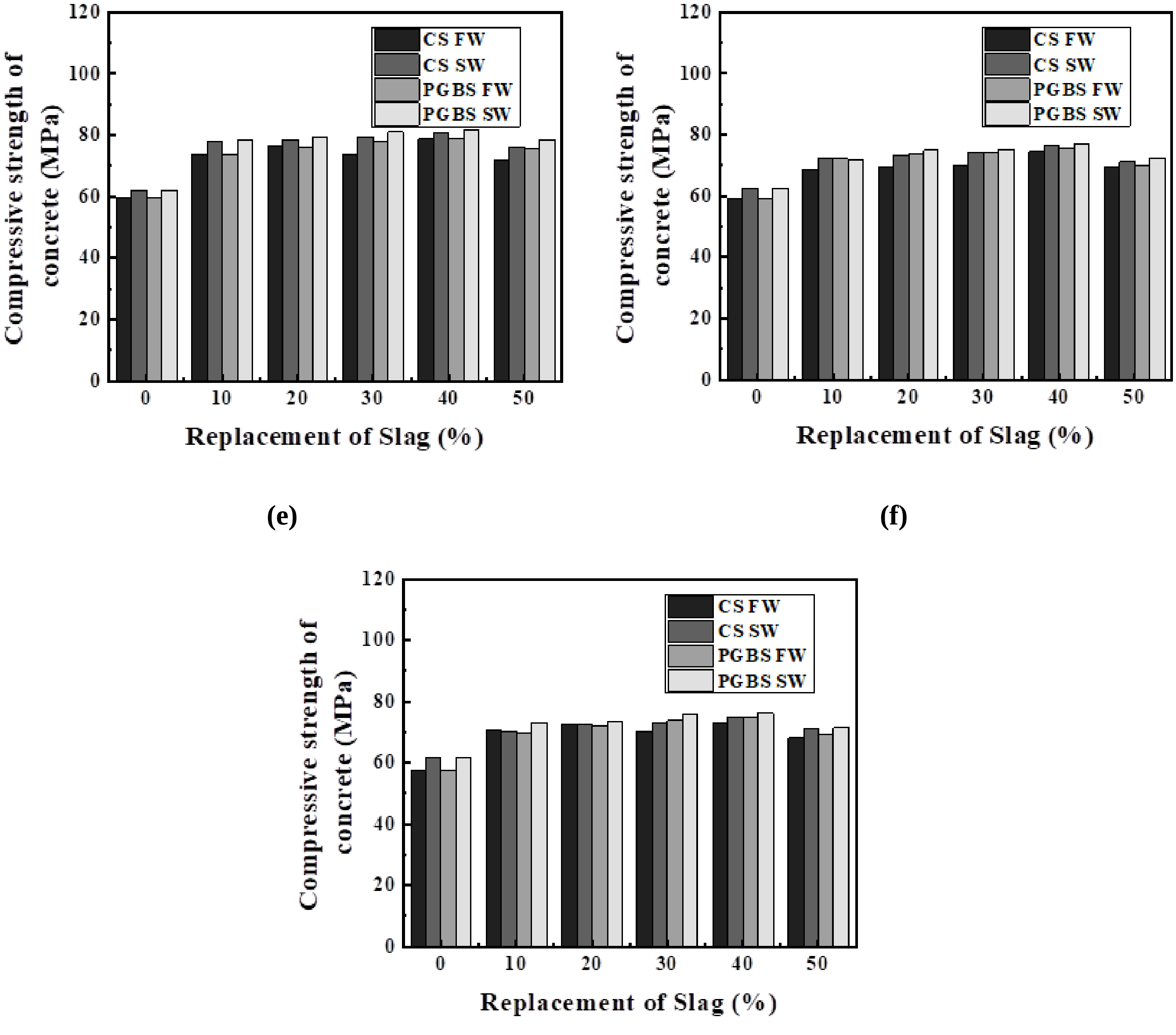
(b)


Compressive strength of concrete (MPa)
Replacement of Slag (%)
0
20
40
60
80
100
120
0
10
20
30
40
50
CS FW
CS SW
PGBS FW
PGBS SW

(c)


Compressive strength of concrete (MPa)
Replacement of Slag (%)
0
20
40
60
80
100
120
0
10
20
30
40
50
CS FW
CS SW
PGBS FW
PGBS SW

(d)



(e)

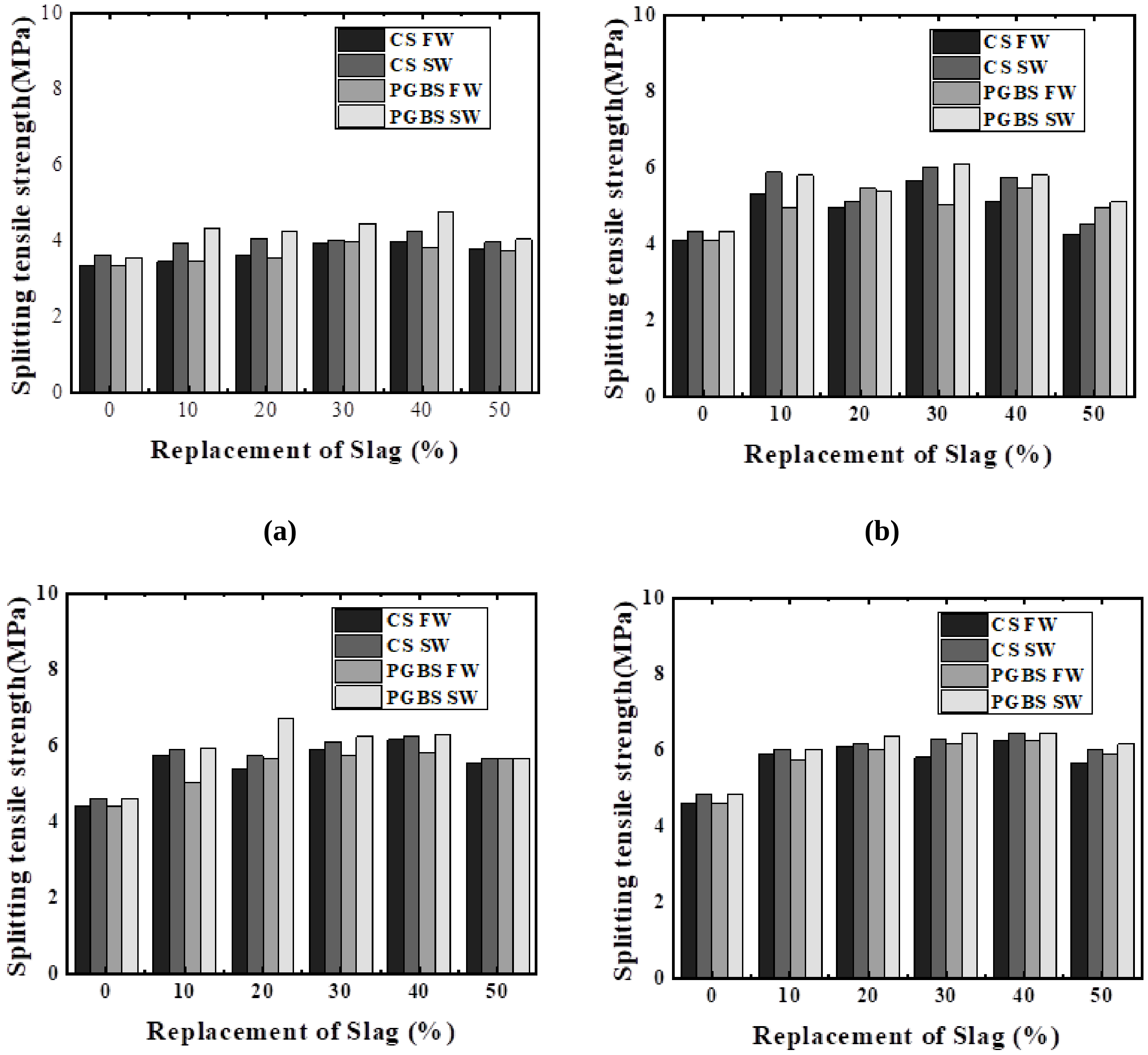
(f)

(g)

Figure 4.7 Compressive strength of concrete (MPa) at different curing periods. (a) 7 days (b) 28 days (c) 56 days (d) 90 days (e) 180 days (f) 270 days (g) 365 days

4.4 SPLITTING TENSILE STRENGTH OF CONCRETE

The figure. 4.8 (a to g) shows the split tensile strength results. It was observed that the PGBS aggregates provide a slightly higher strength at 28 days as compared to the CS aggregates. There are only limited studies on the use of PGBS aggregates in concrete. The marginally higher strength observed at 28 days for PGBS concrete maybe because of the higher reactivity of PGBS as compared to the CS aggregates. This may have resulted in more C-S-H forming at 28 days as compared to CS aggregates, thereby enhancing its strength at 28 days but resulting in a similar compressive and split tensile strength at the later ages.

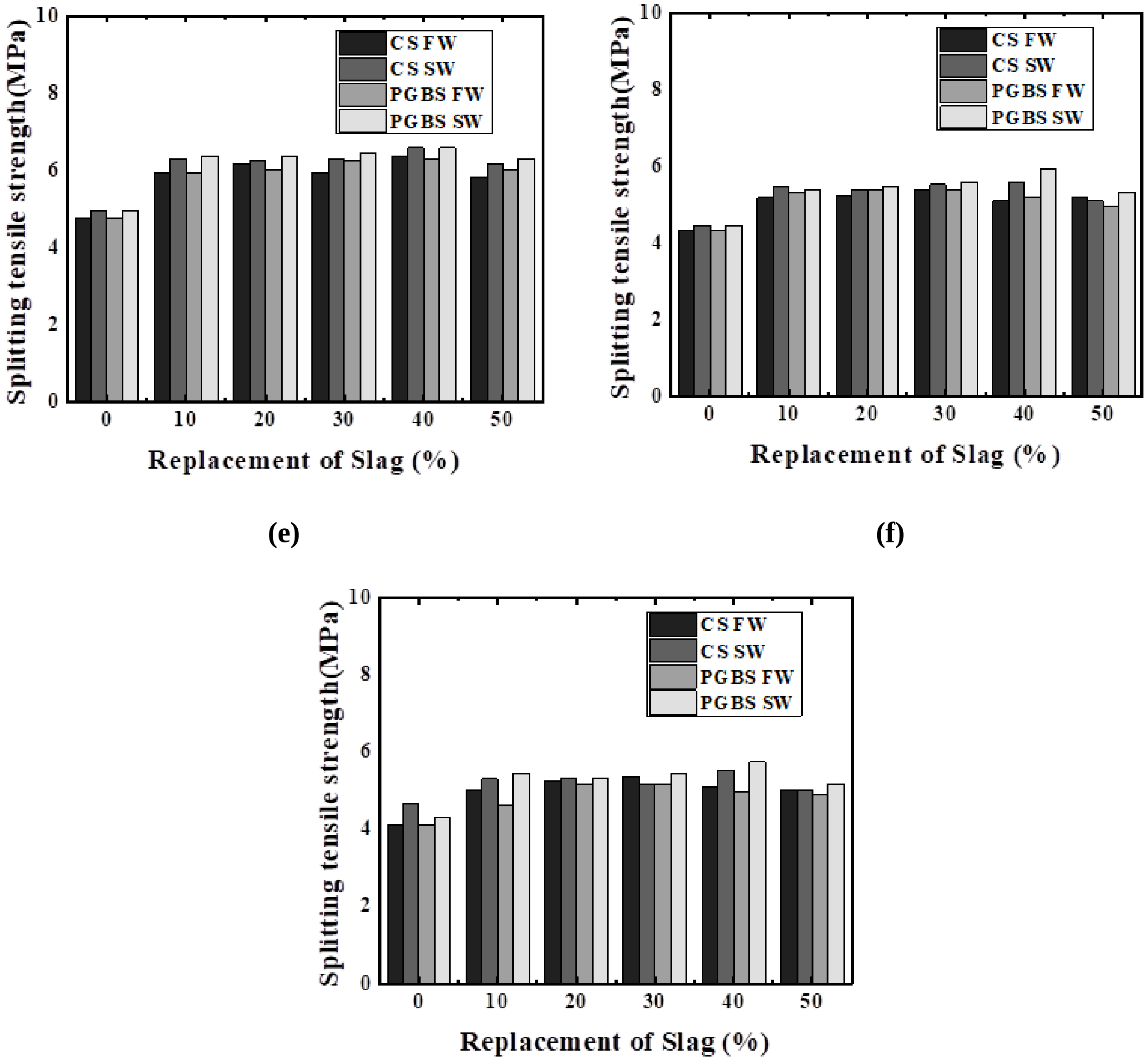


(a)

(b)

(c)

(d)



(e)

(f)

(g)

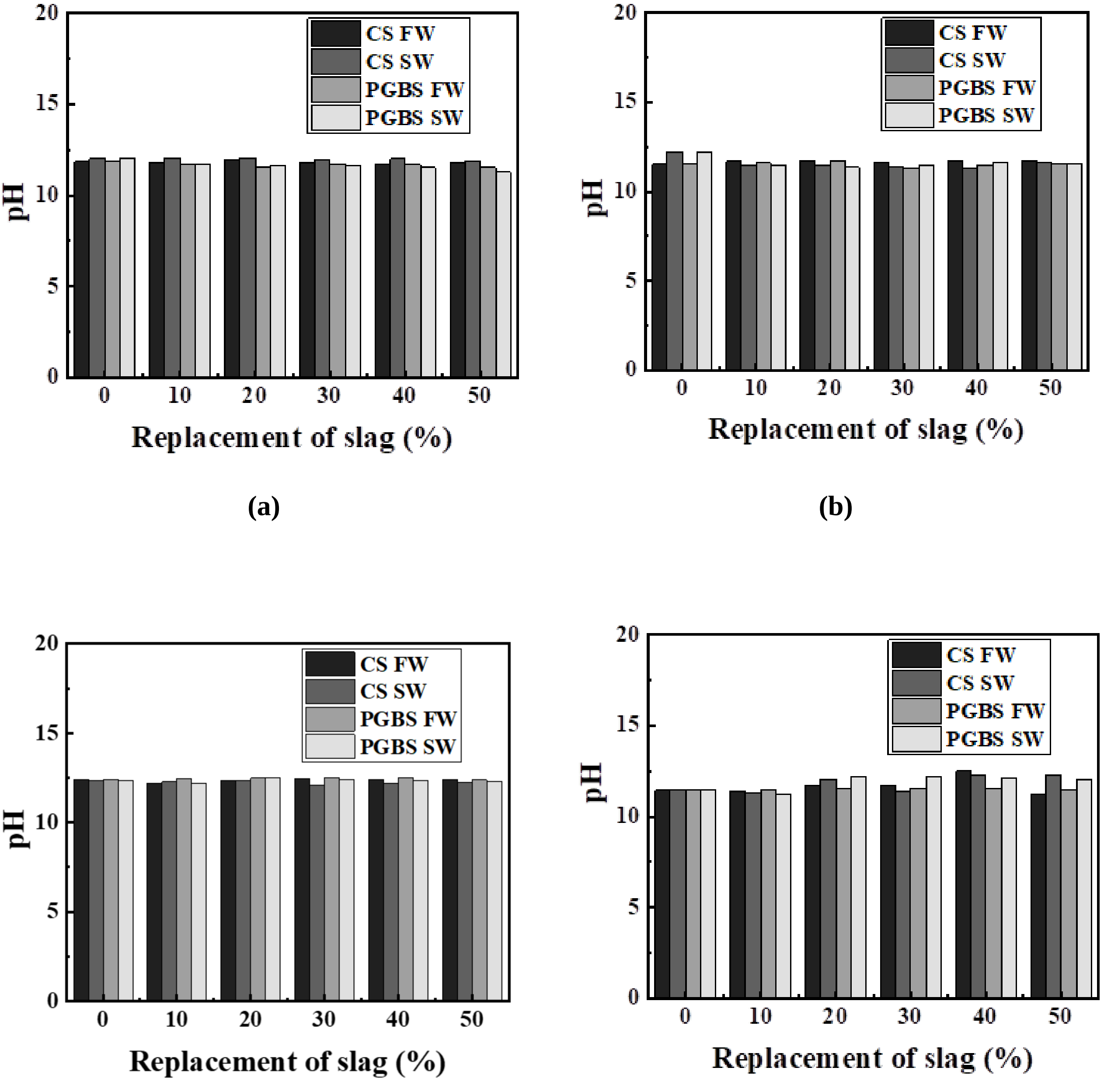
Figure 4.8 Splitting tensile strength of concrete (MPa) at different curing periods. (a) 7 days (b) 28 days (c) 56 days (d) 90 days (e) 180 days (f) 270 days (g) 365 days

4.5 DURABILITY STUDIES OF CONCRETE

Concrete durability properties are closely associated with the conveyance of the material, predominantly in aqueous conditions. Permeability of concrete increases with the increase in the number of cracks permitting the entry of harmful chemicals to pierce deep into the concrete, resulting in weakening of the cement matrix. Seawater has a huge quantity of aggressive agents like magnesium, sulfate, and chloride ions, and carbon dioxide are major constituents that attack the calcium hydroxide, calcium monosulfoaluminate hydrate, and calcium silicate hydrate of hydrated Portland cement, which may lead to serious compromise with the durability of concrete. The durability test was carried out to understand the aggressive effects of seawater on concrete. The toxicity characteristic leaching procedure (TCLP) method was adopted to determine the concentration of chloride, sulphate, and sodium ions in the concrete naturally based on curing exposure conditions.

4.5.1 Determination of pH level in concrete

The Figure. 4.9 (a to g) shows the variation of pH level in concrete. The leached solution was tested for pH to understand the residual pH value of concrete as it would be a direct indicator of chloride ion ingress. After 7 days of curing and subjecting for the leaching process using the TCLP method, it was observed that all combinations of concrete cured both in fresh and seawater had a pH of minimum of 11.5 with partial replacements of CS and PGBS for FA. In the case of 28 days test results, showed that a minimum of 11.3 pH was obtained in all leached solutions. Results of 90 days and 180 days exhibited a slight decrement in pH where a minimum of 11.5 was noted in all solutions. A similar observation was observed for 270 days and 365 days results as the minimum pH obtained were 11.2 and above in all solutions.

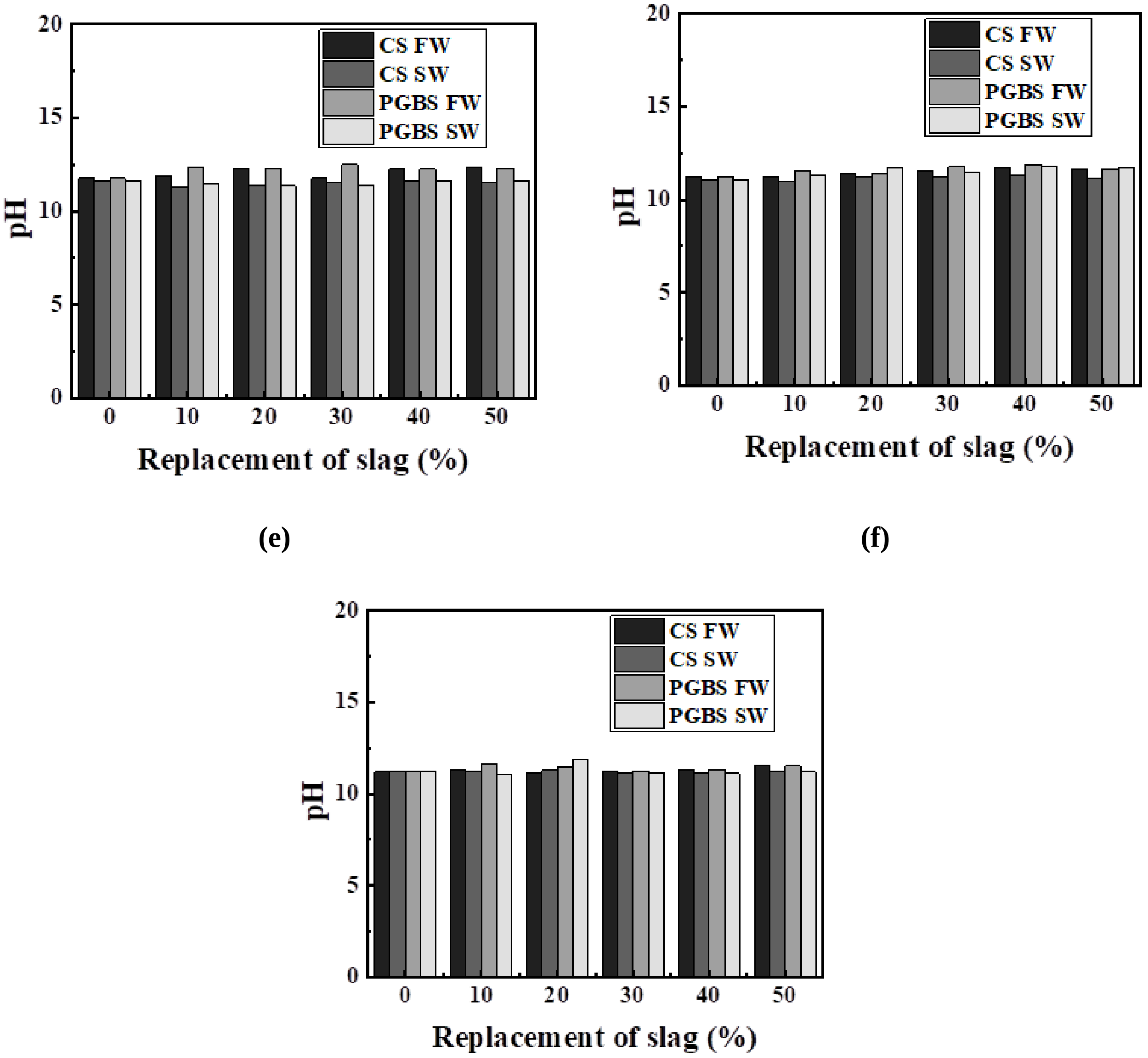

20
15
10
5
0
pH
0
10
20
30
40
50
Replacement of slag (%)
CS FW
CS SW
PGBS FW
PGBS SW

(a)

(b)

(c)

(d)



(e)

(f)

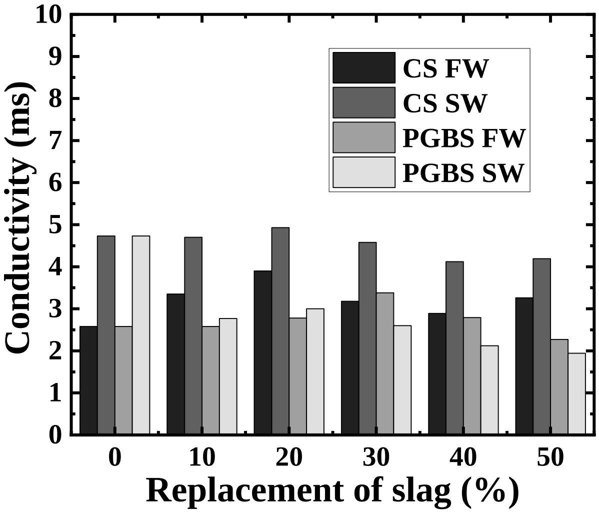
(g)

Figure 4.9 Variation of pH level in concrete. (a) 7 days (b) 28 days (c) 56 days (d) 90 days (e) 180 days (f) 270 days (g) 365 days

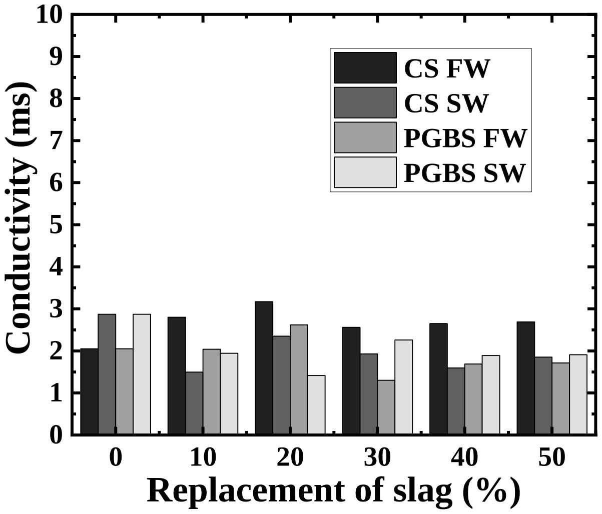
4.5.2 Determination of electrical conductivity in concrete

Figure. 4.10 (a to g) shows the variation of electrical conductivity in concrete. Electrical measurements in cementitious systems are gaining increasing use to quantify the transport properties of concrete mixtures. From Figure. 4.6 In general, the electric conductivity value is higher for all curing ages for specimens cured in seawater. This can attribute to the presence of more ions in seawater as compared to freshwater.

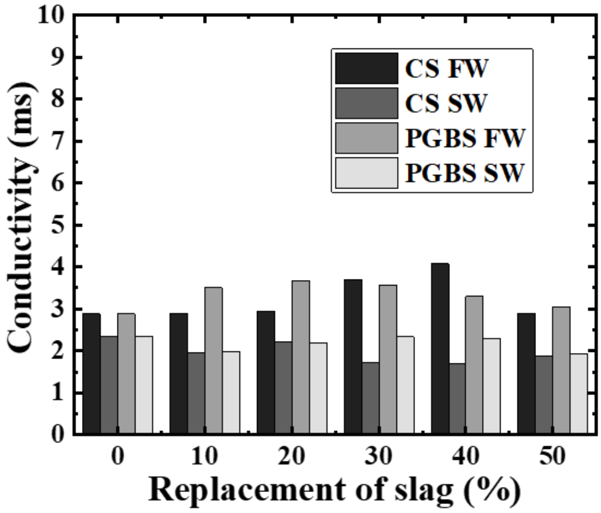
Further, the electrical conductivity test showed the concrete specimens after 7 days of curing have higher conductivity values than electric conductivity values at later ages. This can be attributed to the higher permeability of the concrete specimens at early ages. However, some increase in conductivity values can be observed for specimens cured for 365 days, particularly for seawater cured specimens. This increase in conductivity at the latter ages may be due to the continuous ingress of ions from seawater into concrete with the increase in time of exposure to seawater.



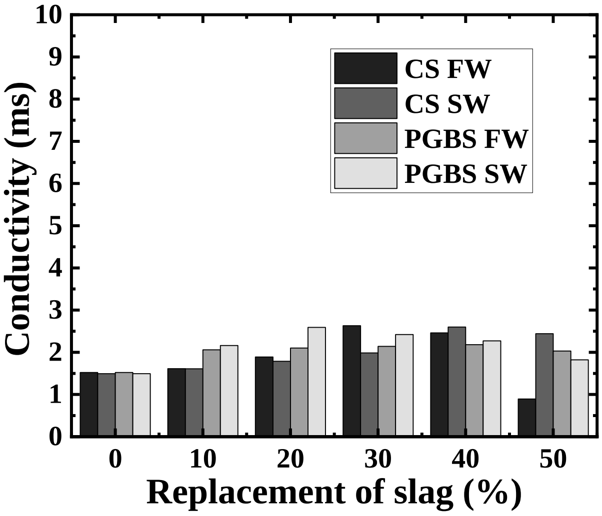
(a)



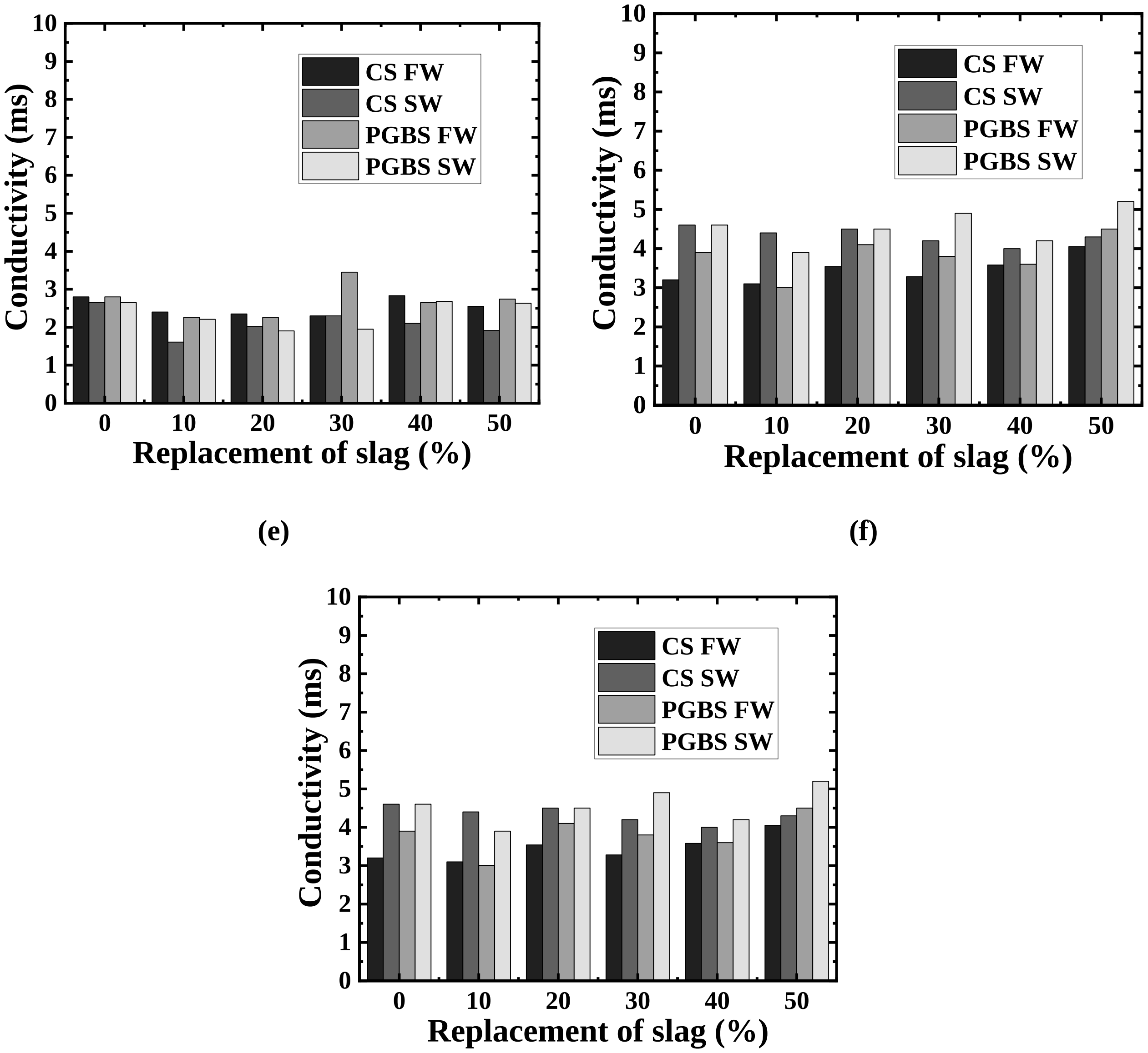
(b)



(c)



(d)



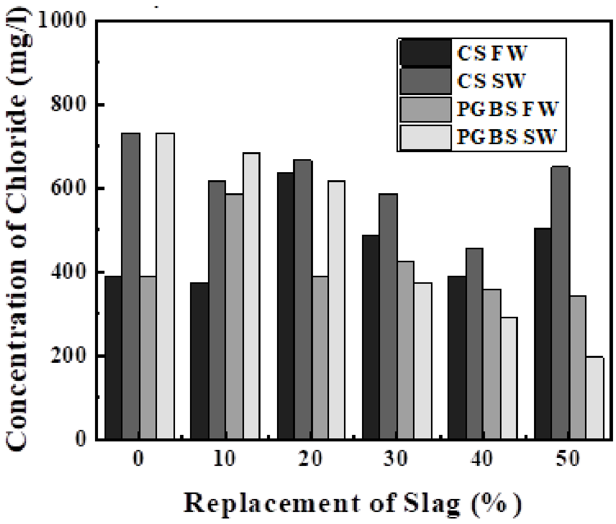
(e) (f)

(g)

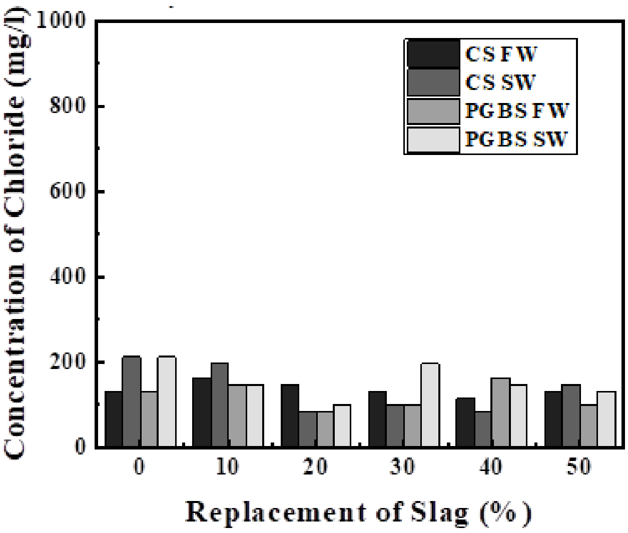
Figure 4.10 Variation of Electrical conductivity in concrete (ms) at different curing periods. (a) 7 days (b) 28 days (c) 56 days (d) 90 days (e) 180 days (f) 270 days (g) 365 days

4.5.3 Determination of chloride concentration in concrete

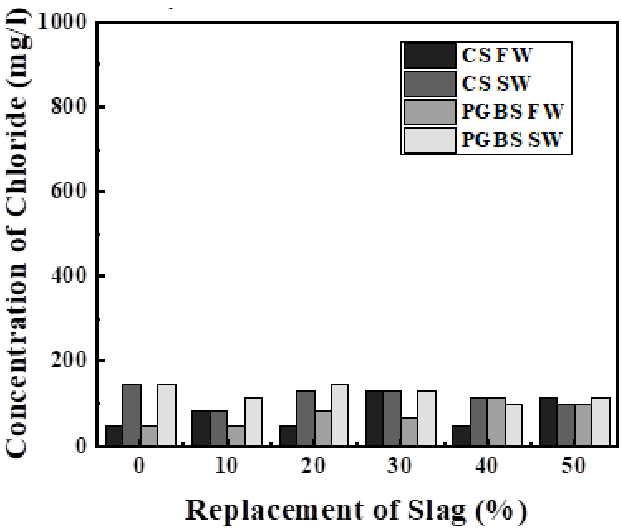
Figure 4.11 (a to g) shows the concentration of chloride in concrete. It was observed that the concrete cured in seawater had a higher concentration of chloride when compared to freshwater cured concrete specimens. At 7 days, the concrete specimens showed the highest chloride concentration, but with the increase in curing period, the concentration was noted. This may be because some of the phases in the hardened cement matrix may try to bind with the chloride ions, thereby reducing the number of free chlorides (Suryavanshi et al., 1997). The C-S-H gel formed may partially counteract chloride migration during the process of hydration by physical adsorption (Suryavanshi et al., 1997). The decrement in chloride concentration observed for seawater curing may also be due to a change in the chloride concentration gradient during the exposure time. Another aspect being noted is that the CS and PGBS concrete had less ingression of chloride when compared to the control mix (FW 0% and SW 0%) after 90 days of curing. But a slight increment was observed after 180 days of curing in the concentration of chloride ions in all CS and PGBS concrete specimens cured in both conditions. Also, PGBS concrete cured in seawater had a higher concentration of chloride when compared to CS concrete. However, it was lesser than the control mix (FW 0% and SW 0%), especially for the concrete specimens with higher compressive strength. In general, the improvement in the chloride ingress for concrete containing slag aggregates can be due to denser microstructure and the lower permeability achieved using the slag aggregates (Suryavanshi et al.,1997). Further, the presence of the slag is also known to promote the formation of Friedel's salt, which binds the chloride ions, hence reducing the total amount of free chlorides (Goni et al., 1994).


Concentration of Chloride (mg/l)
0
200
400
600
800
1000
0
10
20
30
40
50
Replacement of Slag (%)
CS FW
CS SW
PGBS FW
PGBS SW

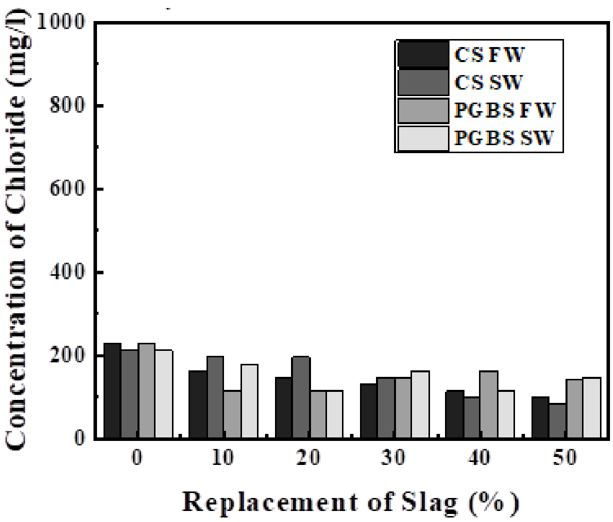
(a)


Concentration of Chloride (mg/l)
0
200
400
600
800
1000
0
10
20
30
40
50
Replacement of Slag (%)
CS FW
CS SW
PGBS FW
PGBS SW

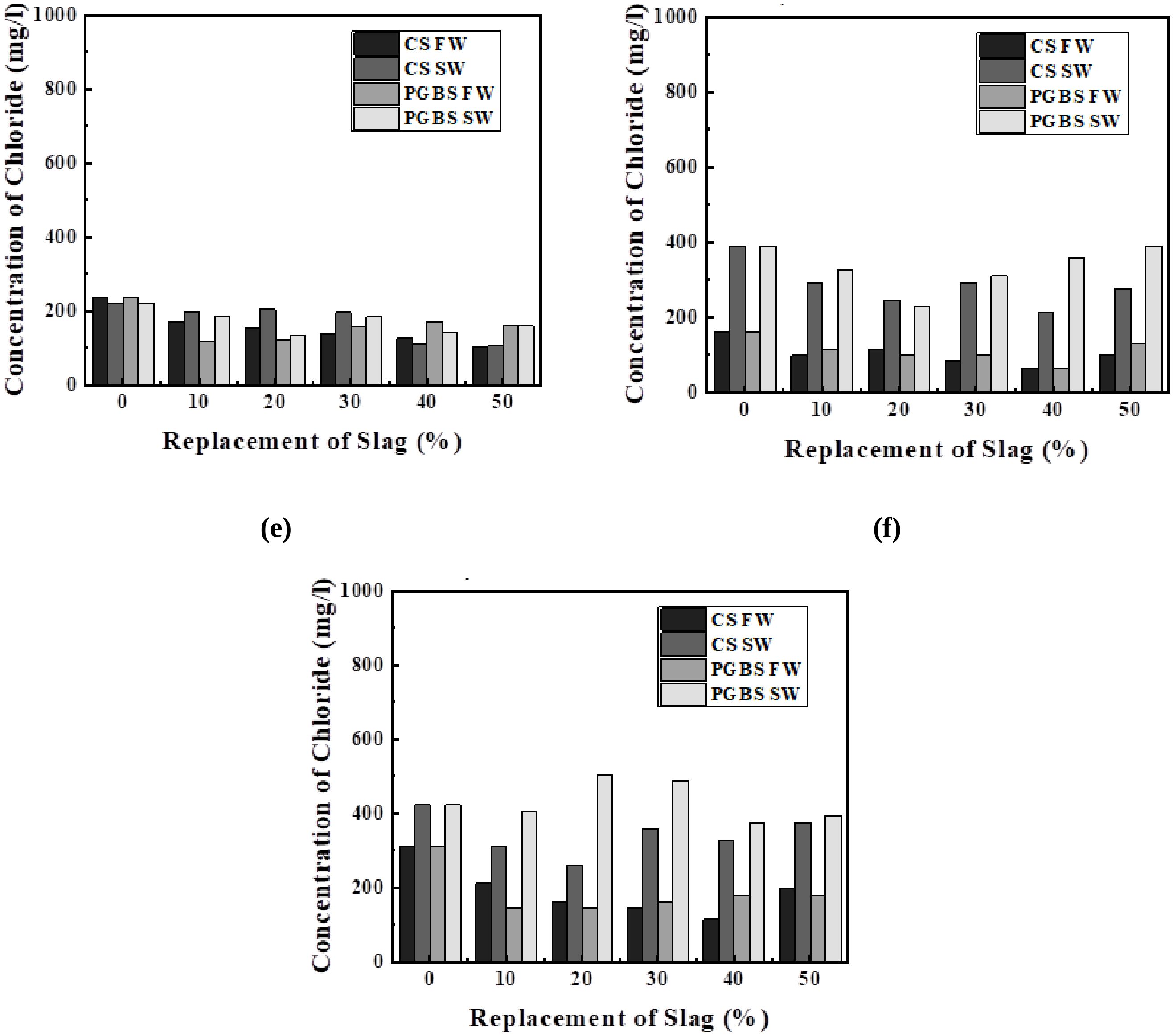
(b)


Concentration of Chloride (mg/l)
0
200
400
600
800
1000
0
10
20
30
40
50
Replacement of Slag (%)
CS FW
CS SW
PGBS FW
PGBS SW

(c)


Concentration of Chloride (mg/l)
0
200
400
600
800
1000
0
10
20
30
40
50
Replacement of Slag (%)
CS FW
CS SW
PGBS FW
PGBS SW

(d)



(e)

(f)

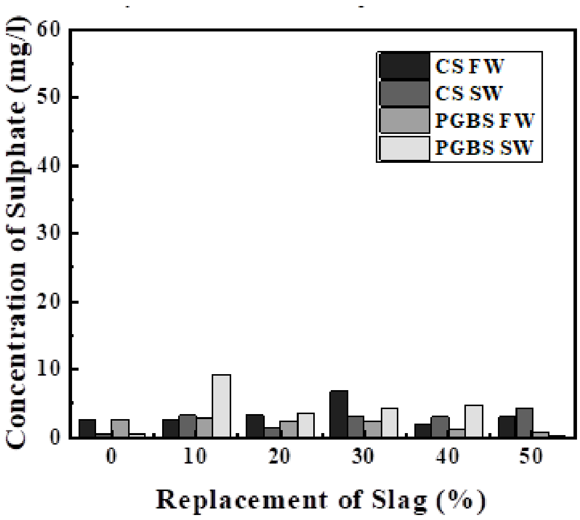
(g)

Figure 4.11 The concentration of chloride in concrete (mg/l) at different curing periods. (a) 7 days (b) 28 days (c) 56 days (d) 90 days (e) 180 days (f) 270 days (g) 365 days

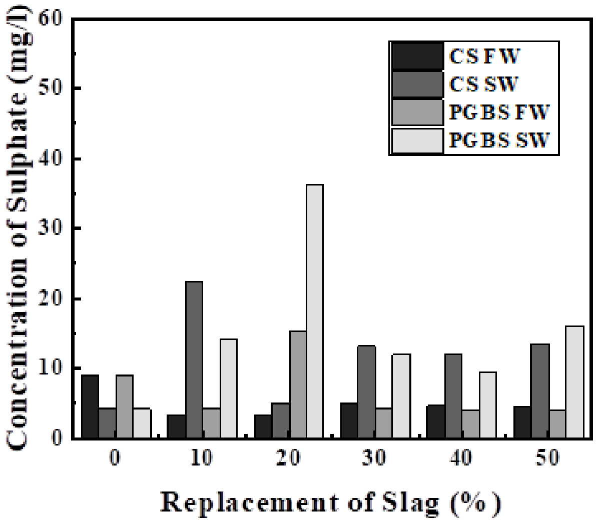
4.5.4 Determination of sulphate concentration in concrete

Figure. 4.12 (a to g) shows the concentration of sulphate in concrete. The sulphate concentration was more up to 28 days of seawater cured specimens. But after 90 days of curing, the concentration of sulphate was more for freshwater curing than seawater. Control mix (FW 0% and SW0%) concrete showed a higher concentration of sulphate when compared to CS and PGBS concrete after 90 days of curing. Also, the concrete that has achieved the highest compressive strength when replaced with CS and PGBS had exhibited less sulfate concentration. However, CS concrete had the highest ingression of sulphate when compared to PGBS concrete when exposed to both curing conditions but less than the control mix. Seawater contains around 2800- 3000 mg/l of SO4- (Chen et al., 2008). In coastal areas, the concrete is continuously exposed to sulphate attack by sulphate ions contributed by calcium, magnesium, and sodium salts (Al-Amoudi et al., 1992 and Rasheeduzzafar, 1998).

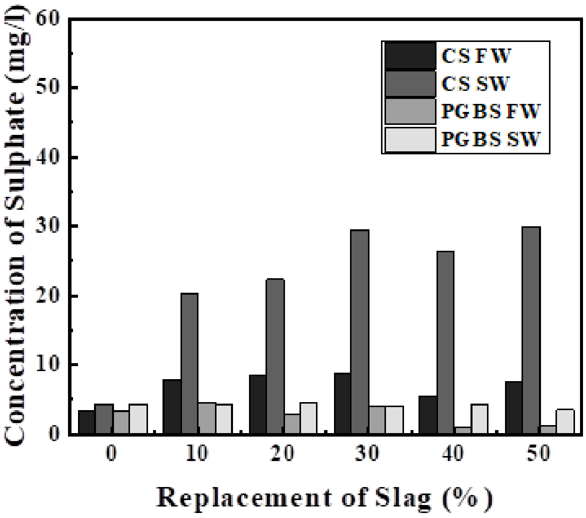
Sulfate attack is usually ascribable to the existence of magnesium sulfate or sodium sulfate, due to the partial solubility of calcium sulfate in water at normal temperatures (i.e., approximately 1400 mg/l SO4-2) (Al-Amoudi et al., 1992). The concentration of sulphate was observed to increase in freshwater due to the presence of sulphates present in tap water. Another important aspect to be noted is the reduction in the sulphate concentration at later ages for the mixtures with both types of slag aggregates, irrespective of the curing condition. This improvement can be attributed to the densification caused by the additional C-S-H formed at the latter ages (Sharma et al., 2017), thereby reducing the permeability of sulphate ions**.**


Concentration of Sulphate (mg/l)
60
50
40
30
20
10
0
CS FW
CS SW
PGBS FW
PGBS SW
0
10
20
30
40
50
Replacement of Slag (%)

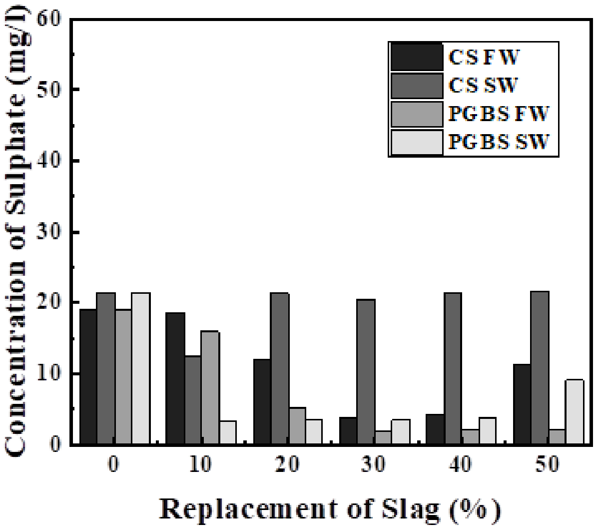
(a)


Concentration of Sulphate (mg/l)
60
50
40
30
20
10
0
CS FW
CS SW
PGBS FW
PGBS SW
0
10
20
30
40
50
Replacement of Slag (%)

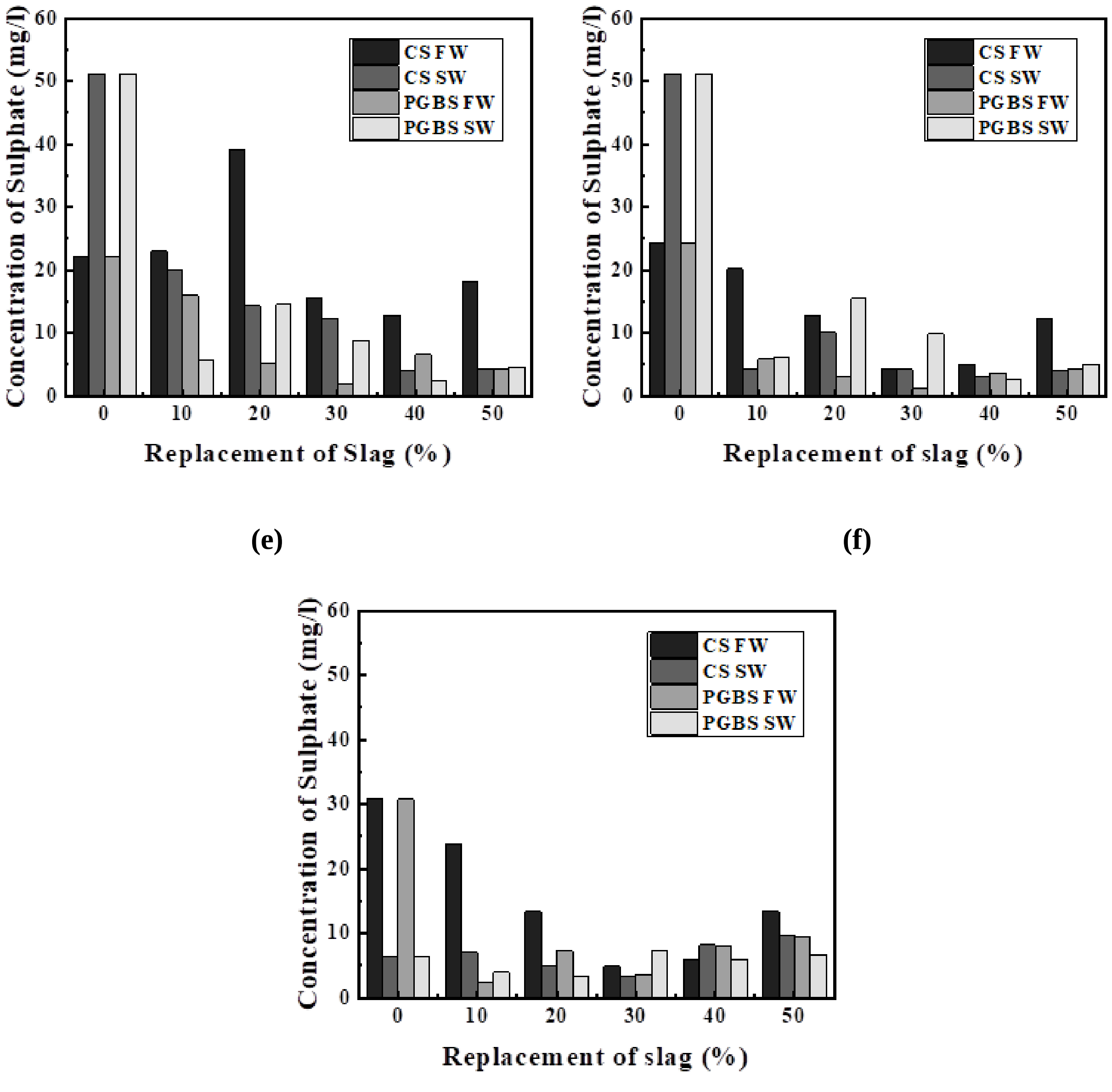
(b)


Concentration of Sulphate (mg/l)
60
50
40
30
20
10
0
CS FW
CS SW
PGBS FW
PGBS SW
0
10
20
30
40
50
Replacement of Slag (%)

(c)


Concentration of Sulphate (mg/l)
60
50
40
30
20
10
0
CS FW
CS SW
PGBS FW
PGBS SW
0
10
20
30
40
50
Replacement of Slag (%)

(d)



(e)

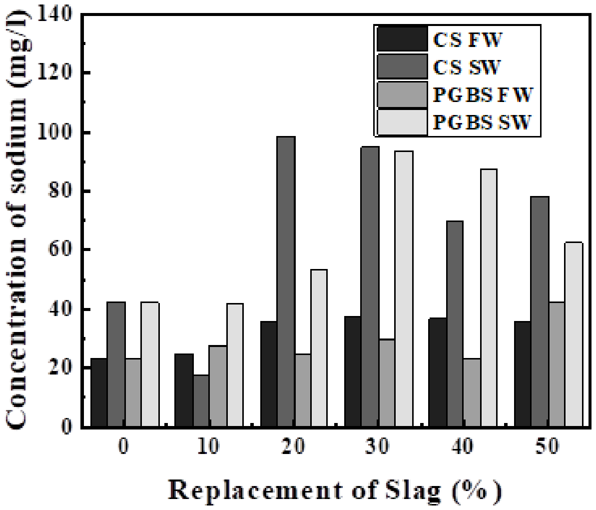
(f)

(g)

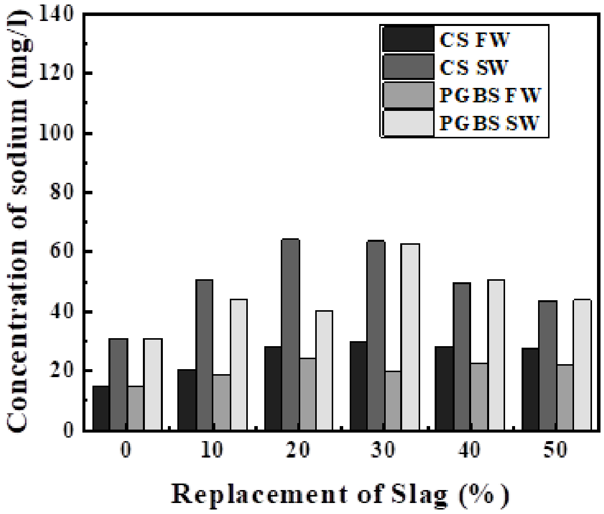
Figure 4.12 The concentration of sulphate in concrete (mg/l) at different curing periods. (a) 7 days (b) 28 days (c) 56 days (d) 90 days (e) 180 days (f) 270 days (g) 365 days

4.5.5 Determination of sodium concentration in concrete

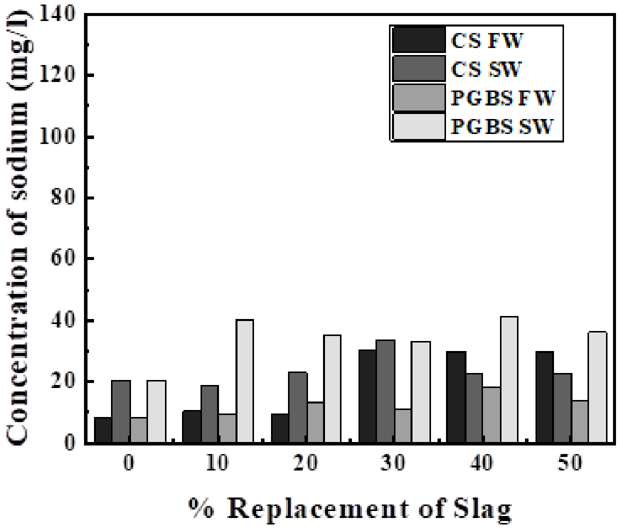
Figure. 4.13 (a to g) shows the concentration of sodium in concrete. The seawater has an average total salinity of 3.5%, typically around 78% is NaCl (Al-Amoudi et al., 1992). Sodium content would be critical as calcium and sodium tend to swap the partners in the chemical reaction. Hence it is essential to understand the quantum of sodium present inside concrete at a given age. The concentration of sodium was high for concrete specimens cured in seawater. PGBS concrete has less ingression of sodium after 90 days of curing in the seawater when compared to CS concrete. PGBS and CS concrete had lesser ingression of sodium when compared to the control mix after 180 days of curing. CS concrete had high ingression of sodium more than PGBS concrete. Therefore, the concrete specimens which had gained the highest compressive strength when replaced by CS and PGBS and cured in both conditions had shown less concentration of sodium ions. This may be due to lower permeability due to the additional C-S-H formation from the hydraulic reaction of the slag aggregates (Sharma et al., 2017).


CS FW
CS SW
PGBS FW
PGBS SW
Concentration of sodium (mg/l)
0
20
40
60
80
100
120
140
0
10
20
30
40
50
Replacement of Slag (%)

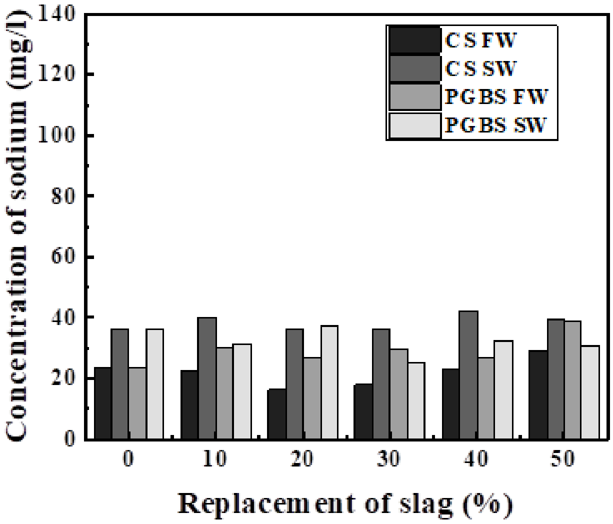
(a)


CS FW
CS SW
PGBS FW
PGBS SW
Concentration of sodium (mg/l)
0
20
40
60
80
100
120
140
0
10
20
30
40
50
Replacement of Slag (%)

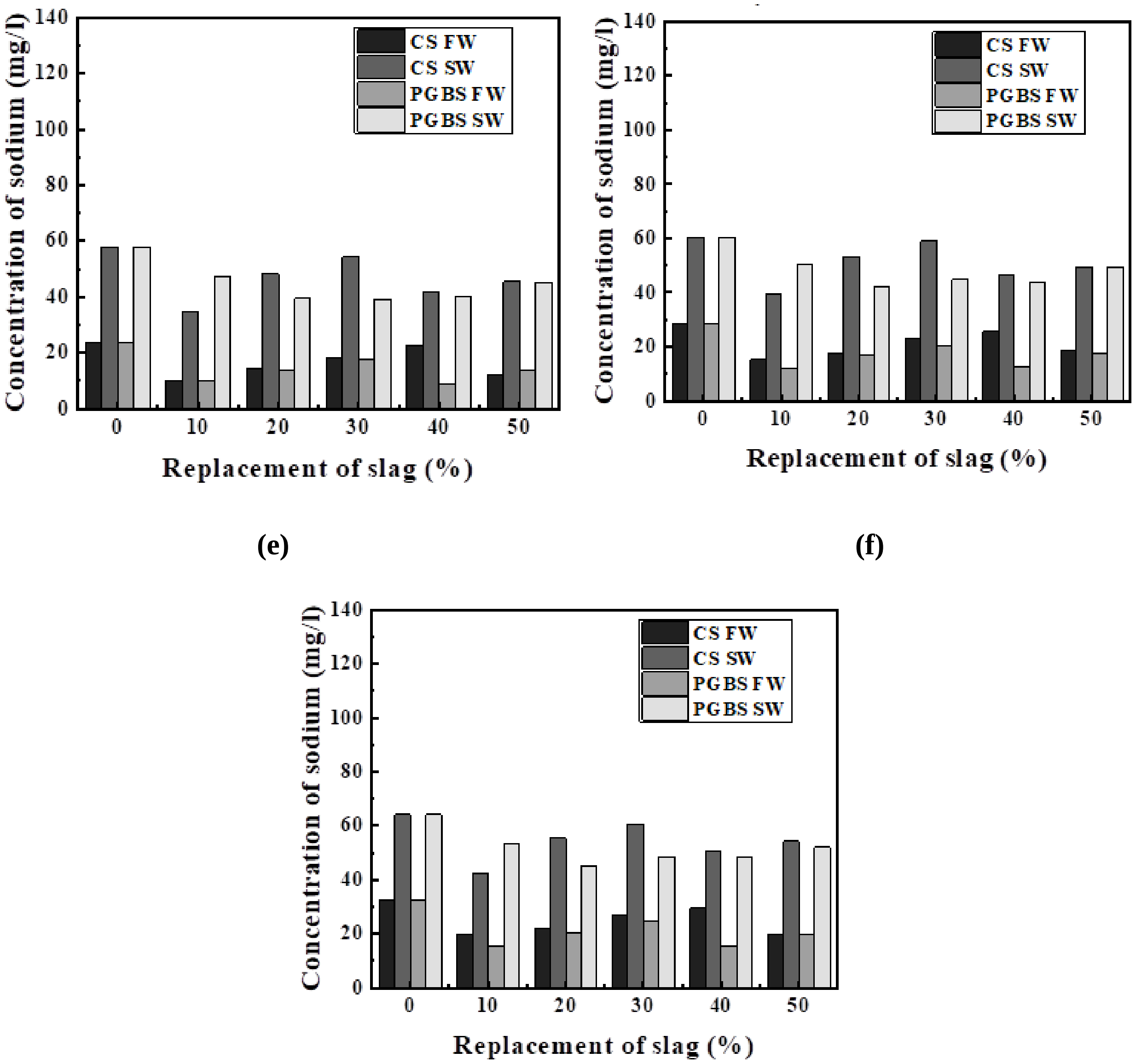
(b)


CS FW
CS SW
PGBS FW
PGBS SW
Concentration of sodium (mg/l)
0
20
40
60
80
100
120
140
0
10
20
30
40
50
% Replacement of Slag

(e)


CS FW
CS SW
PGBS FW
PGBS SW
Concentration of sodium (mg/l)
0
20
40
60
80
100
120
140
0
10
20
30
40
50
Replacement of slag (%)

(d)



(e)

(f)

(g)

Figure 4.13 The concentration of sodium in concrete (mg/l) at different curing periods. (a) 7 days (b) 28 days (c) 56 days (d) 90 days € 180 days (f) 270 days (g) 365 days

4.5.6 CLOSURE

The marsh cone test showed that optimum dosage of SP was obtained for PCE based SP compared to SNF and LS based SP. The compatibility between PCE based SP and PPC mix performed better for less dosage of SP and achieved more flow compared to OPC mixes. Since the w/c ratio and dosage of SP varies with the introduction of fine aggregates to the mixes, the flow table test was performed for mortars to determine the optimum dosage of SP and w/c for CS and PGBS mortars and compared with 100% NFA mortars. The flow table test showed that PPC mix with CS aggregates showed better flow for less w/c and PCE-based SP dosage due to less water absorption of CS aggregates followed y NFA and PGBS mortars. The increase in dosage of SP reduces the w/c and thereby increases the workability of mortars. The concrete cured in seawater achieved more compressive and splitting tensile strength at all ages than freshwater cured concrete specimens. The concrete mix replaced with 40% NFA by CS and PGBS combination attained higher strength than control mix concrete in all conditions. The pH value of concrete was more than 11.5 for all combinations of concrete, and the electrical conductivity values were less especially for CS and PGBS concrete. The concentration of chloride, sulphate, and sodium was less for sea water cured concrete than fresh water, which tried to increase the strength of the concrete.

4.6 MICROSTRUCTURE STUDY OF CONCRETE

The microstructure study of concrete specimens that had attained the highest compressive strength cured under both conditions for 365 days was studied to understand the microstructure variations in concrete better using SEM and EDS analysis. The specimens which achieved highest compressive strength was used for analysis.

4.6.1 Microstructure study of control mix concrete exposed for fresh and seawater curing for 365 days.

The SEM image of control mix concrete cured in fresh water and seawater for 365 days are shown in Figures 4.14 (a, b). The EDS analysis of control mix concrete cured in fresh water and seawater are shown in Figures 4.14 (c, d). The formation of ettringite and $Ca(OH)_2$ was observed in control mix concrete cured in seawater. Some void portion was noticed along with the formation of $Ca(OH)_2$ in the case of control mix concrete cured in freshwater. The concrete cured in seawater was comparatively more than the freshwater cured concrete. However, the concentration of Ca was lesser for control specimens cured in freshwater, and an equal amount of Si was present in specimens irrespective of curing conditions.

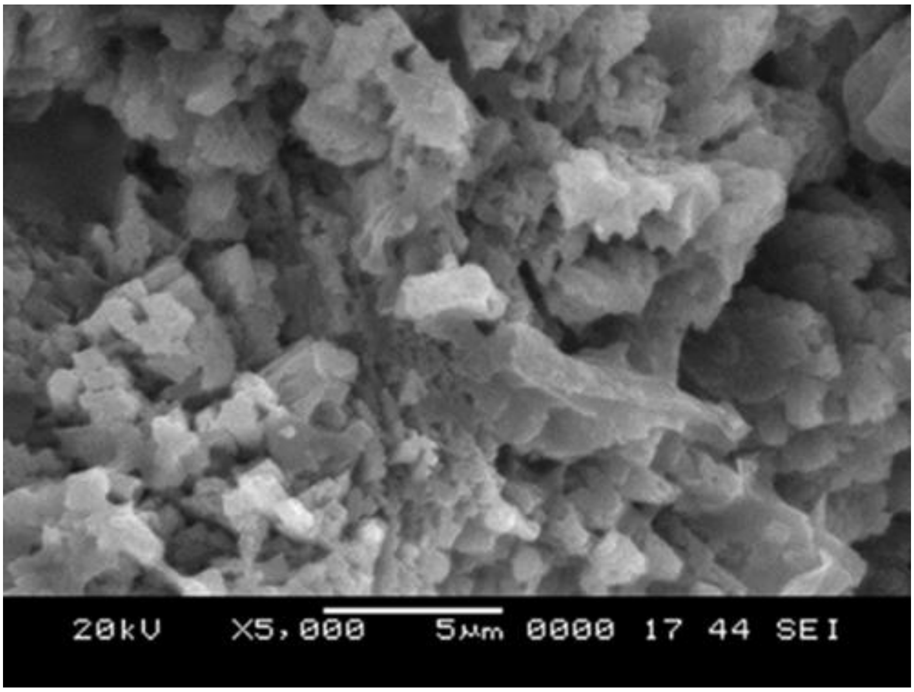


Figure 4.14(a) SEM image of control mix concrete cured in freshwater for 365 days

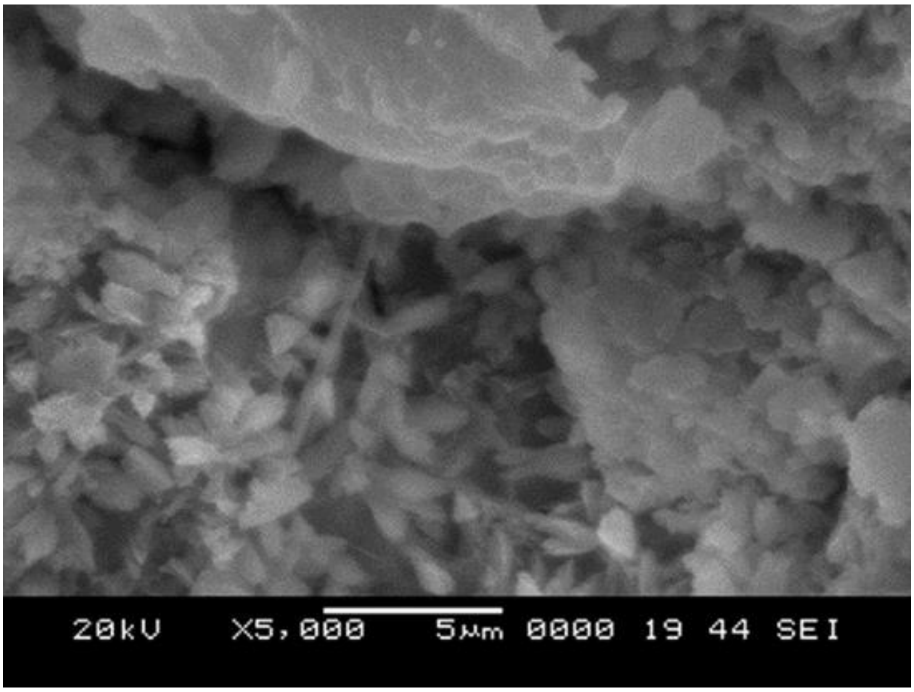


Figure 4.14(b) SEM image of control mix concrete cured in seawater for 365 days

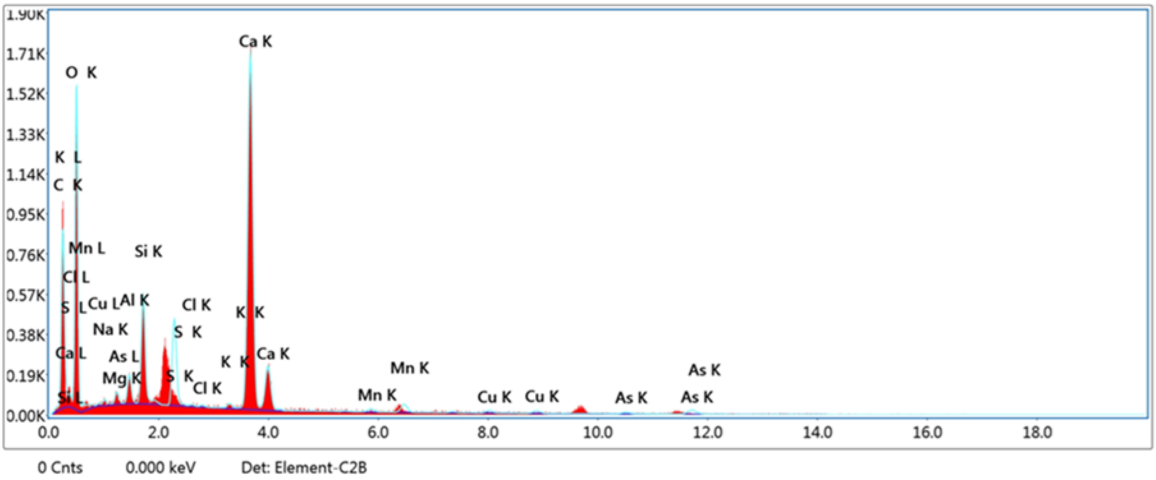


Figure 4.14(c) EDS analysis of control mix concrete cured in freshwater for 365 days

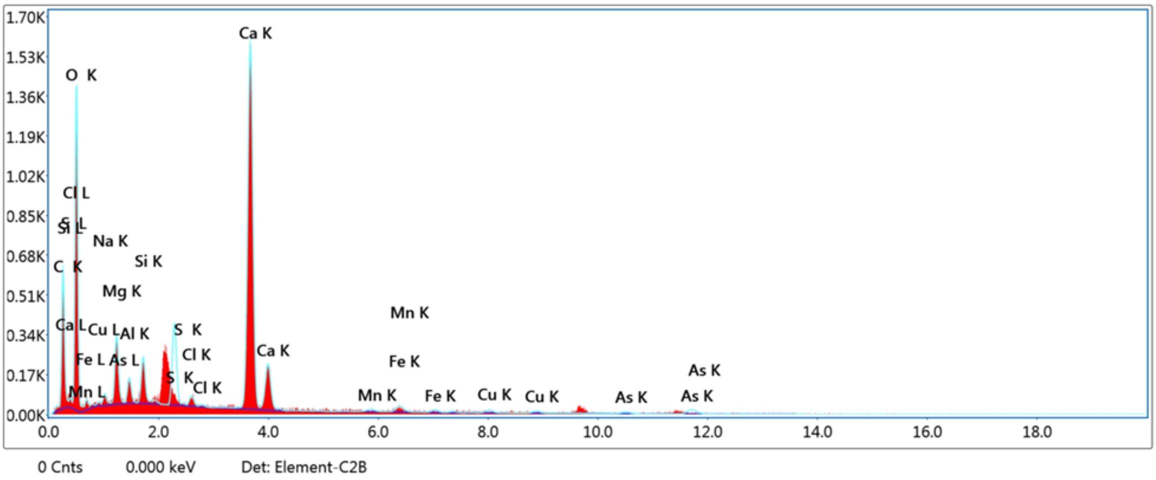


Figure 4.14(d) EDS analysis of control mix concrete cured in seawater for 365 days

4.6.2 Microstructure study of CS concrete exposed for fresh and seawater curing for 365 days

The SEM image of CS concrete cured in fresh water and seawater for 365 days are shown in Figures 4.15 (a, b). The EDS analysis of CS concrete cured in fresh water and seawater are shown in Figures 4.15 (c, d). SEM image depicted the formation of large amount of C-S-H gel which appeared as a dense mass in case of CS SW concrete. The formation of ettringite was observed in CS SW concrete. The amount of Si present in CS SW concrete was more compared to CS FW concrete. This will add on to the mechanical characteristics of seawater cured concrete. The high distribution of less densified C-S-H gel can be observed for CS FW specimens, but seawater specimens showed high densified structures. This may be because of the densification of the microstructures when concrete is cured in seawater. CS concrete has performed better with increased strength properties and exhibiting less chloride (Cl)and sulphate (S) content after subjecting for curing in the sea. The formation of $Ca(OH)_2$ along with the voids in the case of CS FW concrete.

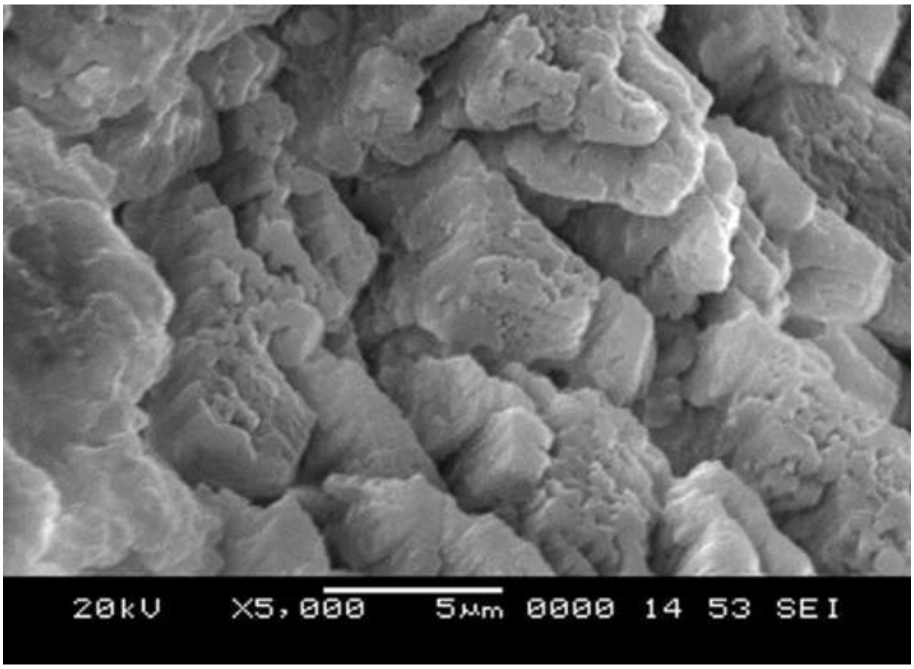


Figure 4.15(a) SEM image of CS FW concrete cured for 365 days

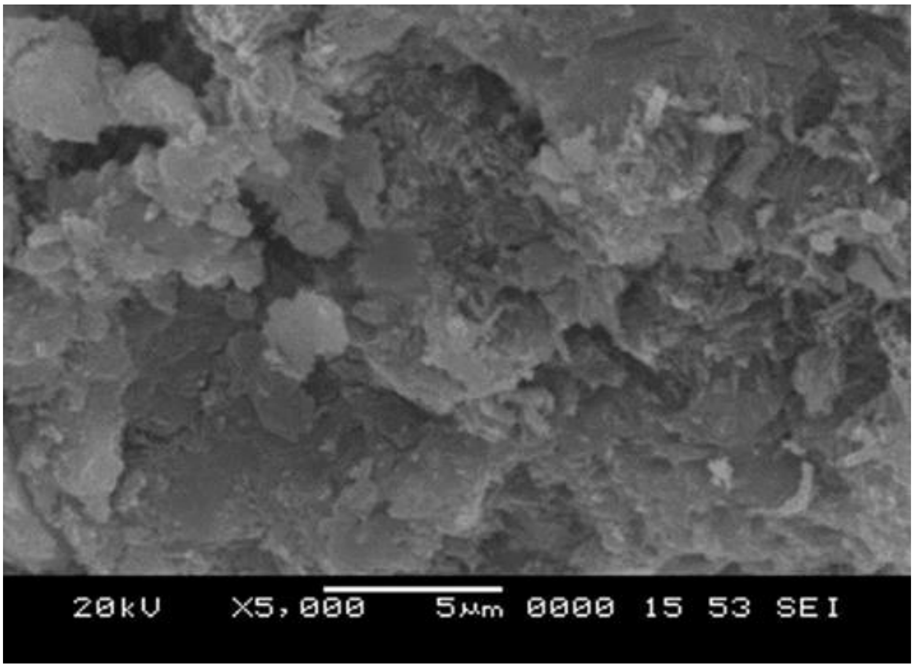


Figure 4.15(b) SEM image of CS SW concrete cured for 365 days

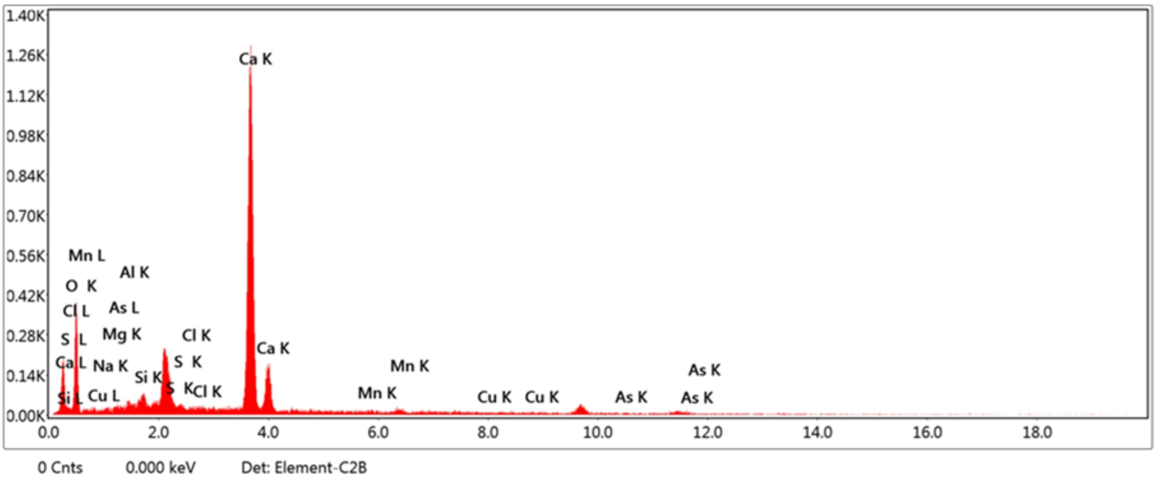


Figure 4.15(c) EDS analysis of CS FW concrete cured for 365 days

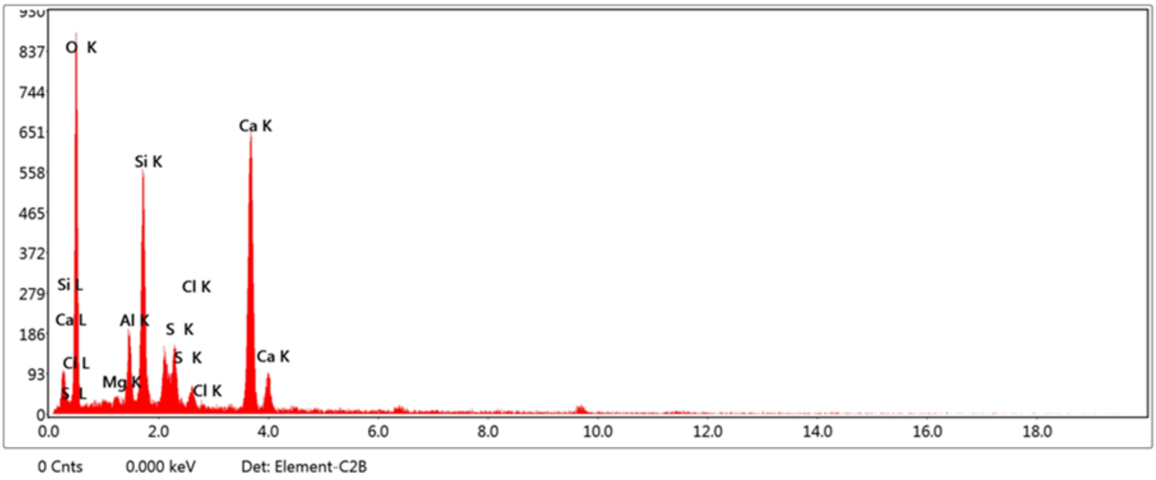


Figure 4.15(d) EDS analysis of CS SW concrete cured for 365 days

4.6.3 Microstructure study of PGBS concrete exposed for fresh and seawater curing for 365 days

The SEM image of PGBS concrete cured in fresh water and seawater for 365 days are shown in Figures 4.16 (a, b). The EDS analysis of PGBS concrete cured in fresh water and seawater are shown in Figures 4.16 (c, d). SEM analysis showed that the matrix appears to be very dense in the case of PGBS SW concrete than PGBS FW concrete due to the formation of C-S-H gel. More amount of $Ca(OH)_2$ have been observed in case of PGBS FW concrete along with some voids. The concentration of Ca was more in PGBS SW concrete whereas in case of PGBS FW concrete the increase in Si concentration was observed.

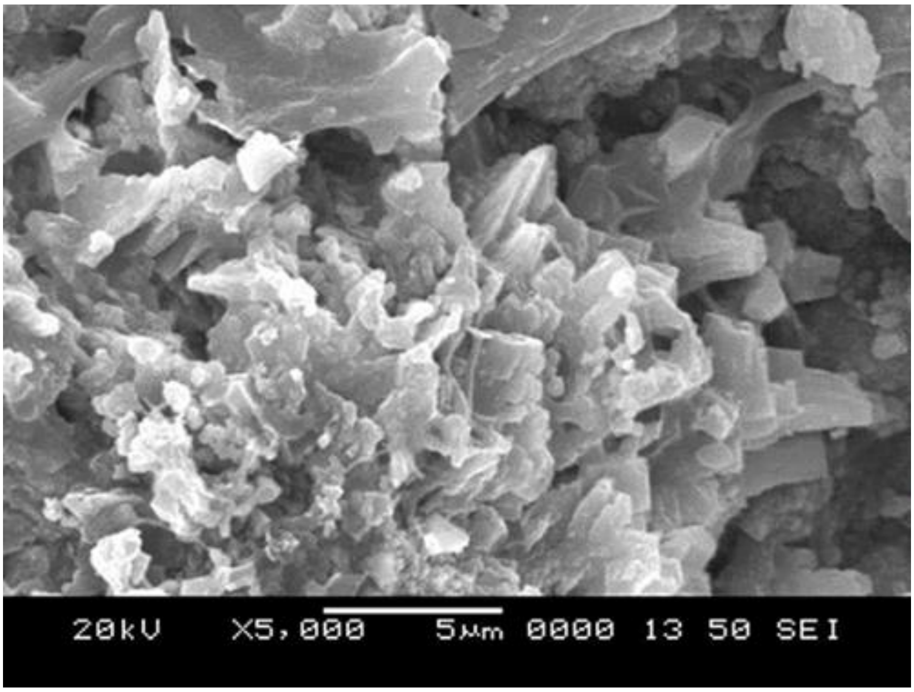


Figure 4.16(a) SEM image of PGBS FW concrete cured for 365 days

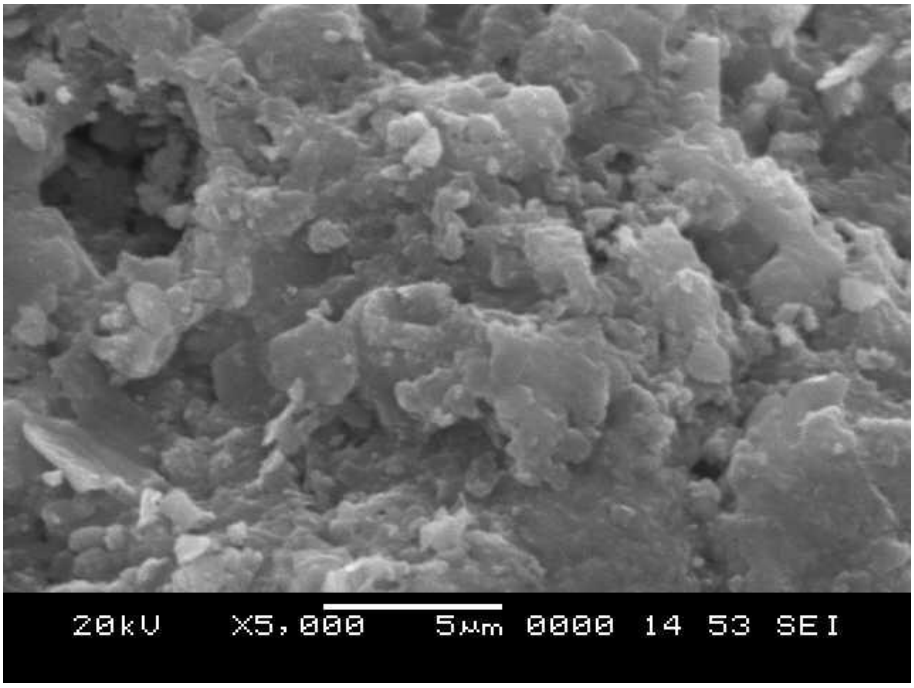


Figure 4.16(b) SEM image of PGBS SW concrete cured for 365 days

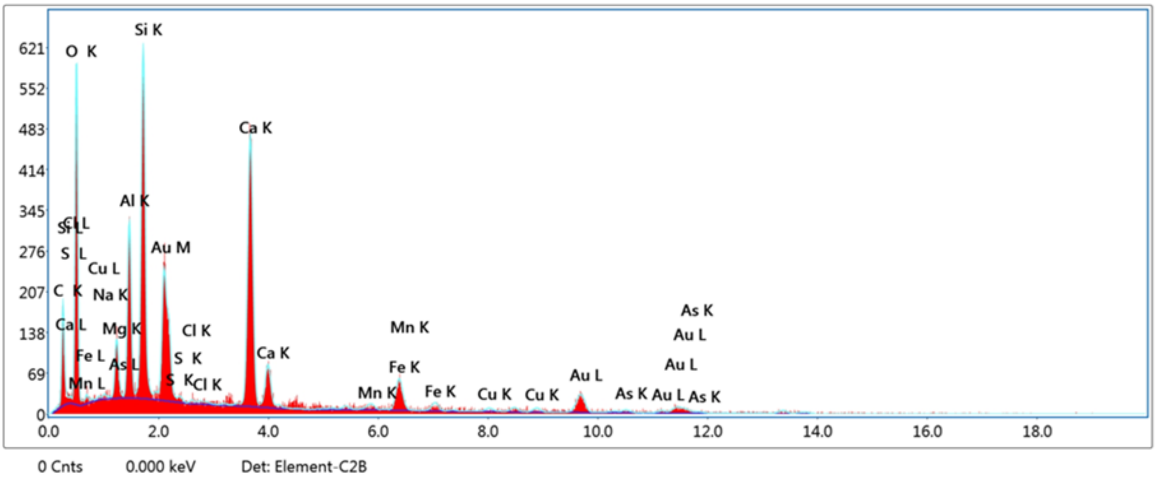


Figure 4.16(c) EDS analysis of PGBS FW concrete cured for 365 days

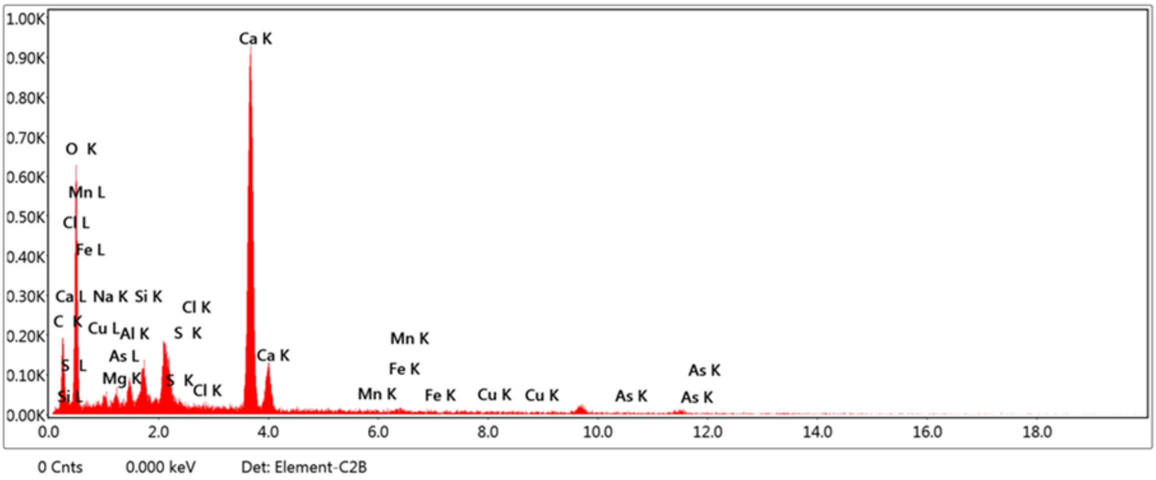


Figure 4.16(d) EDS analysis of PGBS SW concrete cured for 365 days

The concrete's compressive strength depends on the packing of aggregates in the cement matrix and their Interfacial Transition Zones (ITZ). Both CS aggregate hydrated cement paste interface and PGBS aggregate –hydrated cement paste interface showed a comparatively dense ITZ as shown in Figures 4.17 (a) and (b). This densification can be attributed to the additional C-S-H formed at the ITZ from the hydraulic reaction of the slag aggregates. Similar observations have also been reported in previous microstructural studies on slag aggregates (Stevula et al., 1994).

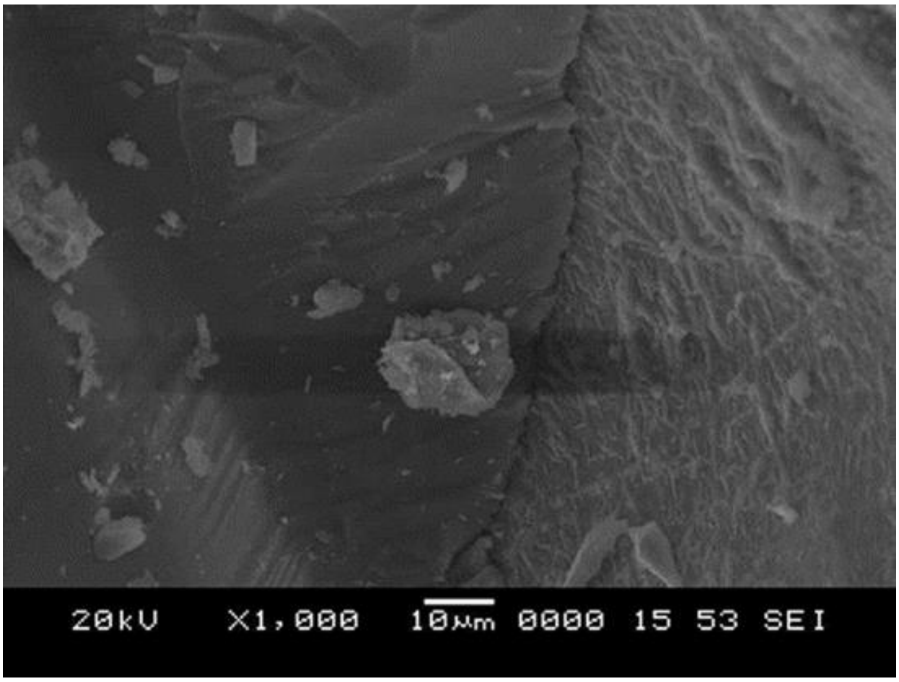


Figure 4.17 (a) SEM micrograph of the interfacial zone and CS aggregate

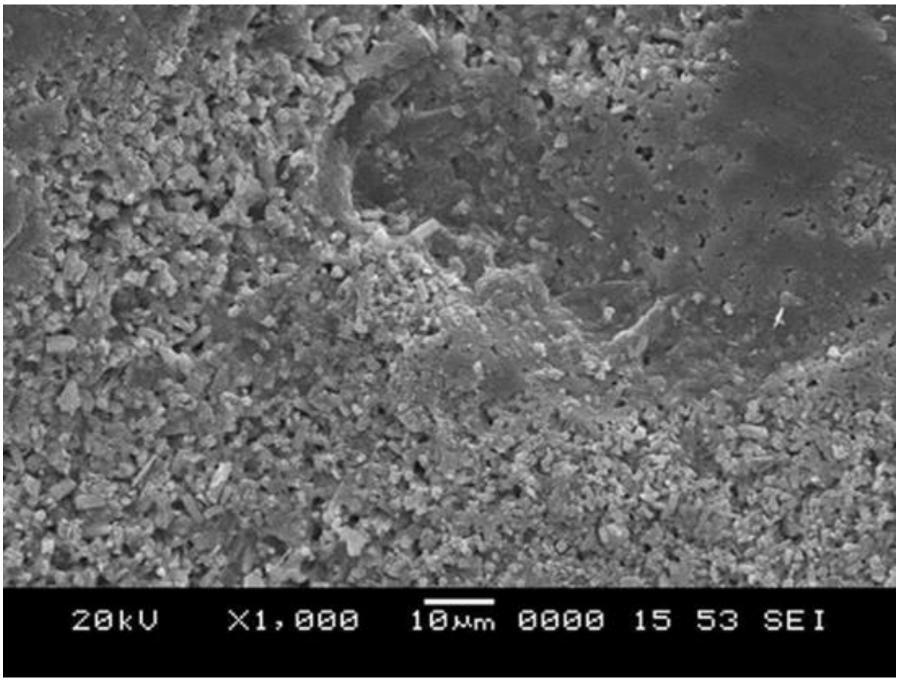


Figure 4.17 (b) SEM micrograph of the interfacial zone and PGBS aggregate

4.7 CLOSURE

Amorphous CaO present in the additive's slag aggregates promotes the growth of additional C–S–H gel which densifies the concrete, particularly at the interfacial transition zone. Cauliflower-like clusters or formless grains of calcium silicate hydrates and crystals of $Ca(OH)_2$ and/or $CaCO_3$ globules were observed in the SEM images of CS and PGBS concrete cured in both conditions. The particles are connected with needles, typical for the acicular C-S-H phases of the cement products in the early stage of hydration. The reduced permeability of concrete contributed to an increase in compressive strength development, which was observed from SEM images, especially in seawater cured specimens.

CHAPTER 5

CONCLUSIONS

5.1 SUMMARY

The durability of concrete is directly affected by its performance in aggressive environments or indirectly by the shape of its porous structure and, consequently, its permeability. Permeability of concrete is the primary index for durability as it affects durability properties such as carbonation, sulphate attack, and alkali-aggregate reaction but regulates the transport of liquid and gaseous phases into concrete. Concrete structures are prone to disintegration when exposed to the marine environment. Therefore, it is important to obtain the right type and good quality aggregate at site because the aggregate form the main matrix of concrete. So, a research gap to investigate the effects of using CS and PGBS as a partial replacement for NFA in concrete in terms of durability aspects was carried out in this work to develop suitable concrete to overcome the effects when immersed in seawater with primary concern to achieve a sustainable environment.

5.2 IMPORTANT CONCLUSIONS FROM THE PRESENT STUDY

1. The marsh cone test indicated that the optimum dosage of SP required for PPC mixes was less compared to OPC mixes. Various trials were carried out for a fixed w/c, exercising various types of SP levels for the cement paste. PCE-based SP showed better performace when compared to SNF and LS-based SP, which appeared inconsistent. The optimum dosage was obtained for the less w/c and less dosage of SP due to good compatibility between PPC and PCE-based SP mixes.

2. In the case of mortars, PPC mixes showed slightly higher flow due to better particle distribution without indication of bleed when compared to OPC. For mortars without SP, the results obtained were reasonably consistent. There was no significant behavior noticed in terms of flow pattern for standard mix and mix with partial replacement of NFA. Also, no remarkable changes in the behaviour of mortars in terms of their green properties were observed.

3. For 50% CS mortars, a slightly higher flow was observed due to less water absorption. But 50% of PGBS mortar demanded more water when compared to other mortar combinations.

4. The flow increased with the addition of SP. An increase in the water indicated higher flow, but the bleed observation started early in the case of 100% NFA and CS mortars. Optimal admixture dosage varied between the paste condition to the mortar flow. However, PCE-based SP's behavior was consistent across the variation and achieved higher flow with a much lesser dosage for both 100% NFA and blended NFA mixes. Though better fresh properties were observed for 0.5 w/c mixes, it may exhibit drastic effects in setting time, gain of strength, and sometimes not set at all.

5. In all the three w/c, it was observed that the mix tends to be more cohesive in the case of CS and PGBS mortar mixes, and there is a significant variation of its percentage flow when compared with 100% NFA mortars. The performance was more consistent in PPC as the particles size distribution was better, and no spikes were observed. The performance was better probably because of the higher specific gravity of CS aggregates.
6. It was observed that a minimum of 0.35 w/c was required for both standard and partial replacement mix to exhibit the reliable flow, which was considered as the initial point for further investigation. Once the optimal dosage was determined, the w/c ratio for PCE based SP became almost constant at 0.40 w/c but demanded a slight variation in the dosage of SP when we compared OPC & PPC mortars.

7. The slump test of concrete showed that CS concrete achieved higher workability compared to control mix and PGBS concrete. The required slump for all the combinations of concrete was attained for optimum dosage of 0.6% PCE based SP and 0.35 w/c as the concrete mix appeared to be more cohesive.

8. The behavior of CS and PGBS concrete showed improved mechanical properties compared to NFA. The mechanical characteristics of CS and PGBS concrete increased with an increase in the curing period when exposed to both seawater and freshwater. This can be attributed to the additional C-S-H formed from the hydraulic reaction of the slag aggregates at the latter ages. Compared to freshwater cured specimens, the seawater cured specimens showed higher compressive strength at early ages, while the ultimate compressive strength was similar for both the curing regimes. This can be attributed to the higher rate of hydration achieved in seawater due to the higher temperature compared to freshwater.
9. For all concrete specimens, the number of free chlorides was initially high but was found to reduce with an increase in the curing age. This may be because of the binding of free chlorides with some of the hydration products at later ages. As expected, the PGBS and CS concrete showed lower chloride ingression due to its reduced permeability as compared to that of NFA concrete.
10. Similarly, the sulphate concentration was also lower for PGBS and CS concrete which can again be attributed to the lower permeability of the CS and PGBS concrete compared to the NFA concrete.
11. Seawater contains a high amount of sodium and makes it more alkaline. Still, the ingression of sodium into the concrete was within limits, and not much variation was seen between PGBS, CS, and NFA concrete. Sodium and calcium have a tendency to swap partners in the chemical reaction. Tests were done to estimate sodium in concrete and thereby understanding the stability of calcium silicates with the concrete over time. The conjugate chemical with sodium would indicate the stability of the chemical composition.

12. SEM analysis showed a denser ITZ at later ages for PGBS and CS concrete. This may be due to the additional C-S-H formed at the aggregate-hydrated cement paste interface from the hydraulic reaction of the slag aggregates.
13. At the outset, the concrete with partial replacement of fine aggregate with PGBS and CS indicates better strength properties when cured in seawater, and chlorides are showing a considerably lower value even after 180 days. These results are seen after the specimen has been placed in the sea. They have undergone both chemical and physical abuse by the sea.
14. The present study shows that more durable and sustainable concrete can be designed for marine applications by partially incorporating suitable low-cost and eco-friendly alternatives in contrast to natural fine aggregate (NFA- river sand).

5.3 CONTRIBUTION

- The new emerging metallic slag aggregates (CS and PGBS) used in this study have shown that the slag aggregates can be successfully utilized in concrete production which can also help to conserve natural materials and reduce the cost of waste treatment before disposal.
- Many key factors have been identified in this research work which plays a vital role to be considered to strengthen the concrete against the action of seawater like the selection of materials based on properties of materials, availability, and economic factors, design of mix proportion for lower water-cement ratio and higher workability.
- Accordingly, the performance of metallic slags, when partially replaced for natural fine aggregates, has tried to reduce the permeability of ions into the concrete. Thereby it's increasing the strength and durability of concrete when exposed to seawater for 365 days.
- The construction industry has always faced the problem concerning compatibility between cement and admixture. In this research work, it was identified that compatibility must not only exist between cement and admixtures but aggregates as

well. Like the shape and size, water absorption of aggregates plays a significant role in concrete mix proportion to develop an excellent durable concrete.

- This research work has tried to resolve the great challenges faced by the concrete industry to serve the two pressing needs of human society, namely environmental protection and trying to meet the infrastructure requirement and consequential needs of urbanization and industrialization.

5.4 LIMITATION OF THE STUDY

- The percentage of slag to be replaced is limited to a maximum replacement of 50% only.
- The production of these slag aggregates in the coastal areas is limited.
- The cost of construction will increase due to increase in the cost of transportation.
- The variation in the properties of sea water leads to the demand of new mix design

5.5 SCOPE FOR FUTURE RESEARCH

- Durability studies along with shrinkage studies can be carried.
- The study can be extended to reinforced concrete structures and carried out for the exact constituents of concrete and mix proportion to determine the future corrosion process.
- The behaviour of the metallic concrete at elevated temperatures can be studies.
- Statistical and numerical analysis can be carried out with extended experiments to validate and forecast the results

REFERENCES

Books/Journals Articles/ Reports

Agullo, L., Toralles-Carbonari, B., Gettu, R., and Aguado, A. (1999). “Fluidity of cement pastes with mineral admixtures and superplasticizer—a study based on the Marsh cone test.” *Mater. Struct.,* 32(7), 479–485.

Al-Jabri, K. S., Al-Saidy, A. H., and Taha, R. (2011). “Effect of copper slag as a fine aggregate on the properties of cement mortars and concrete.” *Constr. Build. Mater.,* 25(2), 933–938.

Al-Jabri, K. S., Hisada, M., Al-Oraimi, S. K., and Al-Saidy, A. H. (2009). “Copper slag as sand replacement for high performance concrete.” *Cem. Concr. Compos.,* 31(7), 483–488.

Al-Amoudi, O. S.B., Abduljauwad, S. N., Rasheeduzzafar, Maslehuddin, M. (1992). " Effect of chloride and sulfate contamination in soils on corrosion of steel and concrete". *Transp. Res. Rec.,* 67–73.

Alter, H. (2005). “The composition and environmental hazard of copper slags in the context of the Basel Convention.” *Resour. Conserv. Recycl.,* 43(4), 353–360.

Ambily, P. S., Umarani, C., Ravisankar, K., Prem, P. R., Bharatkumar, B. H., and Iyer, N. R. (2015). “Studies on ultra-high performance concrete incorporating copper slag as fine aggregate.” *Constr. Build. Mater.,* 77, 233–240.

Anderson, K. W., Uhlmeyer, J. S., and Russell, M. A. (2009). Use of recycled concrete aggregate in PCCP: Literature search.

Arivalagan, S. (2013). “Experimental study on the flexural behavior of reinforced concrete beams as replacement of copper slag as fine aggregate.” *J. Civ. Eng. Urban.,* 3(4), 176–182.

Ayano, T., and Sakata, K. (2000). “Durability of concrete with copper slag fine aggregate.” Spec. Publ., 192, 141–158.

Bahoria, B. V, Parbat, D. K., and Naganaik, P. B. (2013). “Replacement of natural sand in concrete by waste products: A state of art.” *J. Environ. Res. Dev.,* 7(4A), 1651.

Bazant, Z. P. (1979). “Physical model for steel corrosion in concrete sea structures-theory.” *ASCE J. Struct. Div.,* 105(6), 1137–1153.

Berner, R. A. (1975). “The role of magnesium in the crystal growth of calcite and aragonite from sea water.” *Geochim. Cosmochim. Acta*., 39(4), 489–504.

Bharati, S. K., and Chew, S. H. (2016). “Geotechnical behavior of recycled copper slag-cement-treated Singapore marine clay.” *Geotech. Geol. Eng.,* 34(3), 835–845.

Biczok, I., and Blasovszky, N. (1964). Concrete corrosion and concrete protection.

Bilir, T. (2012). “Effects of non-ground slag and bottom ash as fine aggregate on concrete permeability properties.” *Constr. Build. Mater.,* 26(1), 730–734.

Bilir, T., Yüksel, I., Topcu, I. B., and Gencel, O. (2017). “Effects of bottom ash and granulated blast furnace slag as fine aggregate on abrasion resistance of concrete.” *Sci. Eng. Compos. Mater.,* 24(2), 261–269.

Bonen, D. (1992). “Composition and appearance of magnesium silicate hydrate and its relation to deterioration of cement-based materials.*” J. Am. Ceram. Soc.,* 75(10), 2904–2906.

Brindha, D., and Nagan, S. (2011). “Durability studies on copper slag admixed concrete.” *Asian J. Civ. Eng.,* 12(5), 563-578.

Brown, R. D., and Geoghegan, M. P. (1979). “The Corrosion of Concrete Marine Structures.” *Corros. Steel Reinf. Concr. Constr.,* Proc. Conf., London, Feb. 1978, 79–103.

Browne, R. D., Domone, P. L., and Geoghegan, M. P. (1977). “Inspection and monitoring of concrete structures for steel corrosion.” *Offshore Technol. Conf*., Offshore Technology Conference.

Buenfeld, N. R., and Newman, J. B. (1986). “The development and stability of surface layers on concrete exposed to sea-water.” *Cem. Concr. Res.,* 16(5), 721–732.

Burger, S. (2018). “Copper production declined in first ten months of 2017–ICSG. Creamer Media’s Mining Weekly, January 23, 2018.”

Burgos-Montes, O., Palacios, M., Rivilla, P., and Puertas, F. (2012). “Compatibility between superplasticizer admixtures and cements with mineral additions.” *Constr. Build. Mater.,* 31, 300–309.

Butler, A. K., and Harrisson, A. M. (1998). “An investigation of some alternative aggregates for use in concrete.”. *Geol. Soc. Spec. Publ.,* 13(1), 185.

Caliskan, S., and Behnood, A. (2004). “Recycling copper slag as coarse aggregate: hardened properties of concrete.” *Proc. seventh Int. Conf. Concr. Technol. Dev. Ctries.,* 91–98.

Chinmay buddhadev., Jayesh kumar pitroda., Chetna, M,Vyas. (2015). “A review of innovative use of copper slag and foundry sand in design mix concrete” Journal Of International Academic Research For Multidisciplinary, ISSN: 2320-5083, 2(12).

Chavan, R. R., and Kulkarni, D. B. (2013). “Performance of copper slag on strength properties as partial replace of fine aggregate in concrete mix design.” *Int. J. Adv. Engg. Res. Stud.,* 95, 98.

Cherry, B. W., and Kashmirian, A. S. (1983). “Cathodic protection of steel embedded in porous concrete.” *Br. Corros. J.,* 18(4), 194–199.

Cherry, B. W., and Price, S. M. (1978). “Cathodic protection of steel in concrete.” *Corros. Sci*., 18(12), 1091–1094.

Chithra, S., Kumar, S. R. R. S., and Chinnaraju, K. (2016). “The effect of Colloidal Nano-silica on workability, mechanical and durability properties of High-Performance Concrete with Copper slag as partial fine aggregate.” *Constr. Build. Mater.,* 113, 794–804.

Comparet, C., Nonat, A., Pourchet, S., Mosquet, M., and Maitrasse, P. (2003). “The Molecular Parameters and the Effect of Comb-Type Superplasticizers on Self-Compacting Concrete: A Comparison of Comb-Type Superplasticizer Adsorption onto a Basic Calcium Carbonate.” *Spec. Publ.,* 217, 195–210.

Conjeaud, M. L. (1980). “Mechanism of sea water attack on cement mortar.” *Spec. Publ.,* 65, 39–62.

Dash, M. K., Patro, S. K., and Rath, A. K. (2016). “Sustainable use of industrial-waste as partial replacement of fine aggregate for preparation of concrete–A review.” *Int. J. Sustain. Built Environ.,* 5(2), 484–516.

Davenport, W. G., King, M., Biswas, A. K., and Schlesinger, M. (2002). Extractive Metallurgy of Copper: Pergamon.

Diamond, S. (2004). “The microstructure of cement pastes and concrete—a visual primer.” *Cem. Concr. Compos.,* 26(8), 919–933.

Diamond, S. (2005). “The patch microstructure in concrete: effect of mixing time.” *Cem. Concr. Res.,* 35(5), 1014–1016.

Dongxue, L., Xinhua, F., Xuequan, W., and Mingshu, T. (1997). “Durability study of steel slag cement.” *Cem. Concr. Res.,* 27(7), 983–987.

Erlin, B., and Verbeck, G. J. (1975). “Corrosion of metals in concrete-needed research.” *Spec. Publ.,* 49, 39–46.

Finley, H. F. (1961). “Corrosion of reinforcing steel in concrete in marine atmospheres.” *Corrosion.,* 17(3), 104t-108t.

Friedland, R. (1950). “Influence of the quality of mortar and concrete upon corrosion of reinforcement.” *J. Proc.,* 125–139.

Ftikos, C., and Parissakis, G. (1985). “The combined action of Mg2+ and Cl− ions in cement pastes.” *Cem. Concr. Res.,* 15(4), 593–599.

Ganiron Jr, T. U. (2013). “Use of recycled glass bottles as fine aggregates in concrete mixture.” *Int. J. Adv. Sci. Technol.,* 61, 17–28.

Glasser, F. P., Marchand, J., and Samson, E. (2008). “Durability of concrete—Degradation phenomena involving detrimental chemical reactions.” *Cem. Concr. Res.,* 38(2), 226–246.

Gomes, P. C. C., Gettu, R., Agullo, L and Bernad, C. (2001). “Experimental optimization of high strength self-compacting concrete.” *Proceedings of Second International Symposium on SCC.,* 377-386.

Gonçalves, J. P., Tavares, L. M., Toledo Filho, R. D., Fairbairn, E. M. R., and Cunha, E. R. (2007). “Comparison of natural and manufactured fine aggregates in cement mortars.” *Cem. Concr. Res.,* 37(6), 924–932.

Gorai, B., and Jana, R. K. (2003). “Characteristics and utilisation of copper slag—a review.” *Resour. Conserv. Recycl.,* 39(4), 299–313.

Griffin, D. F. (1967). “Tests on reinforced concrete-salt gain accelerates corrosion of steel.” *Mater. Prot.,* 6(7), 39.

Guyot, R., Rant, R., and Varizat, A. (1983). “Comparison of the resistance to sulfate solutions and to sea water of different portland cements with or without secondary constituents.” *Spec. Publ.,* 79, 453–470.

Goni, S., Ma, P. Lorenzo., Sagrera, J.L. (1994). "Durability of hydrated Portland cement with copper slag addition in NaCl+ Na2SO4 medium". *Cem. Conc.Res.*, 24(8), 1403-1412.

Hausmann, D. A. (1964), “Electrochemical behaviour of steel in concrete”, *A. C. I.,* 171.

HuseyinYigiter., Halit Yazıcı., Serdar Aydın. (2007). "Effects of cement type,water/cement ratio and cement content on sea water resistance concrete". *Build Environ.,* 42 (4), 1770-1776.

Houston, J. T., Atimtay, E., and Ferguson, P. M. (1972). Corrosion of reinforcing steel embedded in structural concrete. Center for Highway Research, University of Texas at Austin.

Hwang, B.G., Leong, L. P., and Huh, Y.K. (2013). “Sustainable green construction management: Schedule performance and improvement.” *Technol. Econ. Dev. Econ., 19(sup1.),* S43–S57.

Hwang, C.-L., and Laiw, J.C. (1989). “Properties of concrete using copper slag as a substitute for fine aggregate.” *Spec. Publ.,* 114, 1677–1696.

Jain, M. K., and Pal, S. C. (1998). “Utilisation of industrial slag in making high performance concrete composites.” *Indian Concr. J.,* 72(6), 307–315.

Jau, W.-C., and Tsay, D.-S. (1998). “A study of the basic engineering properties of slag cement concrete and its resistance to seawater corrosion.” *Cem. Concr. Res.,* 28(10), 1363–1371.

Jayasree, C., and Gettu, R. (2008). "Experimental study of the flow behaviour of superplasticized cement paste. *Mater. Struct.,* 41, 1581–1593.

Jayasree, C., and Gettu, R. (2010). “Correlating properties of superplasticised paste, mortar and concrete.” *Indian Concr. J.,* 84(7), 7–18.

Kawano, H. (2002). “The state of using by-products in concrete in Japan and outline of JIS/TR on recycled concrete using recycle aggregate.” *Proc. ls, fib Congr. Sess.*

Khanzadi, M., and Behnood, A. (2009). “Mechanical properties of high-strength concrete incorporating copper slag as coarse aggregate.” *Constr. Build. Mater.,* 23(6), 2183–2188.

Kumar, A., Roy, D. M., and Higgins, D. D. (1987). “Diffusion through concrete.” *Concr.J.,* 21, 31–32.

Kumar, D. S., Kumar, P., Sah, R., Kaza, M., and Prasad, S. M. R. (2016). “Converting Granulated Blast Furnace Slag into Fine Aggregate.” *Int. J. Civ. Eng. Res.,* 7(2), 91–103.

Li, V. C., and Yang, E.-H. (2007). “Self-healing in concrete materials.” *Self-Heal. Mater., Springer,* 161–193.

Lorenzo, M., Goni, S., and Guerrero, A. (2003). “Role of aluminous component of fly ash on the durability of Portland cement-fly ash pastes in marine environment.” *Waste Manag.,* 23(8), 785–792

Liu, H. K., Tai, N. H., and Lee, W. H. (2002). “Effect of seawater on compressive strength of concrete cylinders reinforced by non-adhesive wound hybrid polymer composites.” *Compos. Sci. Technol.,* 62(16), 2131–2141.

Malagavelli, V., and Paturu, N. R. (2012). “Strength and Workability Characteristics of Concrete by using Different super plasticizers.” *Int. J. Mater. Eng.,* 2(1), 7–11.

Mavroulidou, M. (2017). “Mechanical properties and durability of concrete with water cooled copper slag aggregate.” *Waste Biomass Valori.,* 8(5), 1841–1854.

McCoy, W. (1966). “Mixing and curing water for concrete.” Significance Tests Prop. *Concr. Concr. Mater.,* ASTM International.

Mehta, P. K. (1991). Concrete in the marine environment. Elsevier Applied Science New York.

Mehta, P. K., and Monteiro, P. J. M. (2017). Concrete microstructure, properties and materials.

Method 1311: Toxicity Characteristic Leaching Procedure (Report). Washington, DC: U.S. Environmental Protection Agency (EPA). July 1992. Part of "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods."

Murali, B. (2019). Concrete Technology by M S Shetty.

Mohammed Tarek Uddin, Hidenori Hamada, Toru Yamaji. (2004). “Performance of seawater – mixed concrete in the tidal environment.” *Cem. Concr. Res.,* 34(4), 593-601.

Nadeem, M., and Pophale, A. (2013). “Granular Slag-Potential Sustainable Material Alternative to Fine Aggregate in Construction Applications.” *Gazi Univ. J. Sci.,* 26(2), 269–278.

Najimi, M., and Pourkhorshidi, A. R. (2011). “Properties of concrete containing copper slag waste.” *Mag. Concr. Res.,* 63(8), 605–615.

Neville, A. M. (1995). Properties of concrete. Longman London.

Obla, K. H., Hill, R. L., Thomas, M. D. A., Shashiprakash, S. G., and Perebatova, O. (2003). “Properties of Concrete Containing Ultra-Fine Fly Ash.” *ACI Mater. J.,* 100(5), 426–433.

Palin, D., Wiktor, V., and Jonkers, H. M. (2015). “Autogenous healing of marine exposed concrete: Characterization and quantification through visual crack closure*.” Cem. Concr. Res.,* 73, 17–24.

Pappu, A., Saxena, M., and Asolekar, S. R. (2007). “Solid wastes generation in India and their recycling potential in building materials.” *Build. Environ.,* 42(6), 2311–2320.

Poovizhi, T., and Kathirvel, P. (2015). “Behaviour of concrete with partial replacement of copper slag as cement and fine aggregate.” *Trans. Eng. Sci,* 3(2), 30–35.

Prasad, P. S., and Ramana, G. V. (2016). “Feasibility study of copper slag as a structural fill in reinforced soil structures.” *Geotext. Geomembranes,* 44(4), 623–640.

Puertas, F., Santos, H., Palacios, M., and Martínez-Ramírez, S. (2005). “Polycarboxylate superplasticiser admixtures: effect on hydration, microstructure and rheological behaviour in cement pastes.” *Adv. Cem. Res.,* 17(2), 77–89.

Ramezanianpour, A. A., Sivasundaram, V., and Malhotra, V. M. (1995). “Superplasticizers: Their Effect on the Strength Properties of Concretes Made with ASTM Type I and V Cements.” *Concr. Int.,* 17(4), 30–35.

Rasheeduzzafar. (1989). " Durability requirements of concrete construction in the Gulf region with an appraisal of the ACI code". In: Keynote Lecture, 1st Regional Conference in Civil Engineering, Bahrain 29.

Reinhardt, H.-W., and Jooss, M. (2003). “Permeability and self-healing of cracked concrete as a function of temperature and crack width.” *Cem. Concr. Res.,* 33(7), 981–985.

Resende, C., Cachim, P.B., Bastos, A.M., (2008). "Copper slag mortar properties. *Mat.Sci.For.,* 587-588, 862-866.

Rooij, M. De, Tittelboom, K. Van, Belie, N. De, and Schlangen, E. (2013). "Self-healing phenomena in cement-Based materials: state-of-the-art report" of RILEM technical committee 221-SHC: self-Healing phenomena in cement-Based materials. Springer.

Sankh, A. C., Biradar, P. M., Naghathan, S. J., and Ishwargol, M. B. (2014). “Recent trends in replacement of natural sand with different alternatives.” *Proc. Int. Conf. Adv. Eng. Technol.,* 59–66.

Sathyan, D., Anand, K. B., Mini, K. M., and Aparna, S. (2018). “Optimization of superplasticizer in portland pozzolana cement mortar and concrete.” *IOP Conf. Ser. Mater. Sci. Eng.,* IOP Publishing, 12036.

Saxena, P., and Simalti, A. (2015). “Scope of replacing fine aggregate with copper slag in concrete–A review.” *Int. J. Tech. Res. Appl.,* 3(4), 44–48.

Shahiri, J., and Ghasemi, M. (2017). “Utilization of soil stabilization with cement and copper slag as subgrade materials in road embankment construction.” *Int. J. Transp. Eng.,* 5(1), 45–58.

Shanmuganathan, P., Lakshmipathiraj, P., Srikanth, S., Nachiappan, A. L., and Sumathy, A. (2008). “Toxicity characterization and long-term stability studies on copper slag from the ISASMELT process.” *Resour. Conserv. Recycl.,* 52(4), 601–611.

Sharma, R., and Rizwan, A. K. (2017). " Sustainable use of copper slag in self compacting concrete containing supplementary cementitious materials". *J Clean Prod.,* 179-192.

Shayan, A., Xu, A., Chirgwin, G., and Morris, H. (2010). “Effects of seawater on AAR expansion of concrete.” *Cem. Concr. Res.,* 40(4), 563–568.

Shi, C., Meyer, C., and Behnood, A. (2008). “Utilization of copper slag in cement and concrete.” *Resour. Conserv. Recycl.,* 52(10), 1115–1120.

Shi, Z., Shui, Z., Li, Q., and Geng, H. (2015). “Combined effect of metakaolin and sea water on performance and microstructures of concrete.” *Constr. Build. Mater.,* 74, 57–64.

Shoya, M., Aba, M., Tsukinaga, Y., and Tokuhashi, K. (2003). “Frost resistance and air void system of self-compacting concrete incorporating slag as a fine aggregate*.” Spec. Publ.,* 212, 1093–1108.

Shoya, M., Nagataki, S., Tomosawa, F., Sugita, S., and Tsukinaga, Y. (1997). “Freezing and thawing resistance of concrete with excessive bleeding and its improvement.” *Spec. Publ.,* 170, 879–88.

Southwell, C.R., Forgeson, B.W., Alexander, A. L. (1960). " Corrosion of Metals in Tropical Environment." *Corrosion.,* 16 (10), 512–518.

Sudarvizhi, S. M., and Ilangovan, R. (2011). “Performance of Copper slag and ferrous slag as partial replacement of sand in Concrete.” *Int. J. Civ. Struct. Eng.,* 1(4), 918–927.

Supekar, N. (2007). "Utilisation of Copper Slag for Cement Manufacture Construction Management and Review". Sterilite Industries (I) Ltd, Tuticorin.

Stevula, L., Madej, J., Kozankova, J., Madejova, J. (1994). Hydration products at the blast furnace slag aggregate-cement paste interface. *Cem. Concr. Res.,* 413-423.

Suryavanshi, A. K, Swamy, R. N. (1997). "Well-crystalline calcite and amorphous calcite in concrete slabs exposed to long-term atmospheric carbonation". *Adv. Cem. Res.,* 115-125

Swamy, R. N., and Hung, H. H. (1998). “Engineering properties of high-volume fly ash concrete.” *Spec. Publ.,* 178, 331–360.

Szilard, R. (1969). “Corrosion and corrosion protection of tendons in prestressed concrete bridges.” *J. Proc.,* 42–59.

Szilard, R., and Wallevik, O. (1975). “Effectiveness of concrete cover in corrosion protection of prestressing steel.” *Spec. Publ.,* 49, 47–70.

Tang, M., Wang, B., and Chen, Y. (2000). “The research on super high strength, high wearability cement mortar with the incorporation of copper slag as aggregates.” *Concr.J.,* 4, 30–32.

Valcuende, M., Benito, F., Parra, C., and Miñano, I. (2015). “Shrinkage of self-compacting concrete made with blast furnace slag as fine aggregate.” *Constr. Build. Mater.,* 76, 1–9.

Velumani, M., and Nirmalkumar, K. (2014). “Durability and characteristics of copper slag as fine aggregate and fly ash as cement in concrete.” *Second Int. Conf. Curr. Trends Eng. Technol. IEEE.,* 222–227.

Verbeck, G. J. (1975). “Mechanisms of corrosion of steel in concrete.” *Spec. Publ.,* 49, 21–38.

Veritas, B. (1975). Rules and regulations for the construction and classification of offshore platforms. The Bureau.

Wig, R. J., and Ferguson, L. R. (1917). “Reinforced concrete in sea water fails from corroded steel.” *Eng. News-Record.,* 79(15), 689–693.

Wu, W., Zhang, W., and Ma, G. (2010a). “Optimum content of copper slag as a fine aggregate in high strength concrete.” *Mater. Des.,* 31(6), 2878–2883.

Wu, W., Zhang, W., and Ma, G. (2010b). “Mechanical properties of copper slag reinforced concrete under dynamic compression.” *Constr. Build. Mater.,* 24(6), 910–917.

Yeau, K. Y., and Kim, E. K. (2005). “An experimental study on corrosion resistance of concrete with ground granulate blast-furnace slag.” *Cem. Concr. Res.,* 35(7), 1391–1399.

Yüksel, İ., and Bilir, T. (2007). “Usage of industrial by-products to produce plain concrete elements.” *Constr. Build. Mater.,* 21(3), 686–694.

Yuksel, I., and Genç, A. (2007). “Properties of concrete containing nonground ash and slag as fine aggregate.” *ACI Mater. J.,* 104(4), 397.

Yüksel, İ., Özkan, Ö., and Bilir, T. (2006). “Usage of granulated blast furnace slag as fine aggregate in concrete.” *ACI Mater. J.,* 103(3), 203–208.

Yüksel, İ., Siddique, R., and Özkan, Ö. (2011). “Influence of high temperature on the properties of concretes made with industrial by-products as fine aggregate replacement.” *Constr. Build. Mater.,* 25(2), 967–972.

Zhu, Y., Yang, Y., and Yao, Y. (2012). “Use of slag to improve mechanical properties of engineered cementitious composites (ECCs) with high volumes of fly ash.” *Constr. Build. Mater.,* 36, 1076–1081.

LIST OF PUBLICATIONS

Journal Proceedings

1. Thete Swapnil Tanajirao., **Arpitha, D***., Suman, Saha., **Rajasekaran, C.** (2018). "Suitability of quarry dust as a partial replacement of fine aggregate in self-compacting concrete." ***Applied Mechanics and Materials***, 877, 248-253.
2. **Arpitha, D***., **Rajasekaran, C** and Nagesh Puttaswamy. (2018). "Investigations on compatibility of cement-superplasticizer interaction and its influence on mortar workability incorporating copper slag as fine aggregate." In *IOP Conference Series:* ***Materials Science and Engineering***, Vol 431 No.08 p.2009.
3. **Arpitha, D*., Rajasekaran, C**. (2021). "Influence of copper slag properties on behaviour of cement mortars and concrete." ***Lecture Notes in Civil Engineering***, 77, p 649- 657.
4. **Arpitha, D***., Sudarshan, V. J., Thilak Kumar, Y. T., **Rajasekaran, C**. (2021). "Influence of Super-Plasticizers on Blended Cement and their Effect on Flow Characteristics by Incorporating PGBS as Partial Replacement for Fine Aggregates." ***Lecture Notes in Civil Engineering,*** 83, 471- 480.
5. Thilak Kumar, Y.T., **Arpitha, D***., Sudarshan, V. J., **Rajasekaran, C** and Puttaswamy, N. (2021). "Study on Compatibility Issues and Flow behaviour of Copper Slag Based Mortars". ***Lecture Notes in Civil Engineering,*** 83, 751- 758.
6. Sudarshan, V. J., **Arpitha, D***., Thilak Kumar, Y.T. **Rajasekaran, C** and Puttaswamy, N. (2021). "Investigations on flow characteristics of mortars using partial replacement of fine aggregates with Processed granulated blast furnace slag." ***Lecture Notes in Civil Engineering,*** 83, 481- 489.
7. Sudarshan, V.J., **Arpitha, D***., **Rajasekaran, C** and Puttaswamy, N. (2021). "Assessment on performance of Steel slag and PGBS as an alternative for fine aggregate – An assertive review". ***Lecture Notes in Civil Engineering,*** 99, 273- 282.
8. Thilak Kumar, Y. T., **Arpitha, D***., **Rajasekaran, C** and Puttaswamy, N. (2021). "Constructive Scope on Implementation of Copper Slag as Replacement for Natural Fine Aggregate- An Overview". ***Lecture Notes in Civil Engineering***, 99, 263- 272.

9. **Arpitha, D***. and Rajasekaran, C. “Study on Durability Properties of Sustainable Alternatives for Natural Fine Aggregate.” ***Journal of the Institution of Engineers (India): Series A,*** https://doi.org/10.1007/s40030-021-00580-7.
10. **Arpitha, D*, Rajasekaran**, **C**., Pramodkumar Kappadi. (2022). “Study on Processed granulated blast furnace slag as a replacement for fine aggregate for the greener global construction.” ***Lecture notes in civil engineering, Springer Nature*** (*Accepted and In-press*).

Conferences

1. **Arpitha, D*.**, Thilak Kumar, Y. T., Sudarshan, V. J., **Rajasekaran, C** and Nagesh Puttaswamy. ((March 13-15, 2019). “Behaviour Of Mortar with Partial Replacement of Fine Aggregate by Slag in Respect to Green Strength Parameters”.,8th International Engineering Symposium, IES-2019, Kumamoto University, Japan.
2. Sudarshan, V.J., **Arpitha, D***., **Rajasekaran, C** and Nagesh Puttaswamy. (March 13-15, 2019). “Assessment on performance of Steel slag and PGBS as an alternative for fine aggregate – An assertive review”.8th International Engineering Symposium, IES-2019, Kumamoto University, Japan.
3. Thilak Kumar, Y. T., **Arpitha, D*.**, **Rajasekaran, C** and Nagesh Puttaswamy. (March 13-15, 2019) “Constructive Scope on Implementation of Copper Slag as Replacement for Natural Fine Aggregate- An Overview”. 8th International Engineering Symposium, IES-2019, Kumamoto University, Japan.
4. Kondababu K, **Arpitha, D*.** and **Rajasekaran C.** (2020) Durability Studies on Concrete Containing Processed Granulated Blast Furnace Slag (PGBS) as a Partial Replacement of River Sand, *Proc. of Second ASCE India Conference on “Challenges of Resilient and Sustainable Infrastructure Development in Emerging Economies”.* Kolkata.

Journals under review

1. **Arpitha, D***., Thilak Kumar, Y. T., Sudarshan, V. J., **Rajasekaran, C**. (2021). “Performance of mortars with partially replaced iron slag as fine aggregate – A suitable alternative.” ***ICE/ science*** (under process).
2. **Arpitha, D***. and **Rajasekaran, C**. “Compatibility Issues on Performance of Cement Mortars Incorporating Metallic Slags as a Partial Replacement for Fine Aggregates”. ***Indian Concrete Journal***. (Under review).

3. **Arpitha, D*., Rajasekaran, C**. “Processed granulated blast furnace slag - An effective feasible choice to fine aggregates for greener global construction”. ***Indian Concrete Journal***. (Under review).

CURRICULUM VITAE

Name : **ARPITHA, D.**

Contact No : **+91-9740523167**

E-mail : **arpitha.5790@gmail.com**

Date of birth : **05/07/1990**

Address: **#408, 3rd Block, D Group Layout, Andrahalli Main Road, Bangalore -560091**

Education Qualification

Degree	Institution	University	Year of passing	Division
B.E (Civil)	Govt. Sri Krishna Rajendra Silver Jubliee Technological Institute, Bengaluru	VTU	2012	I class
M.Tech (Structural Engineering)	REVA Institute of technology and management Bengaluru	VTU	2014	I class with distinction

Teaching Experience

Organization	Post held	Period
REVA University, Bengaluru	Assistant Professor	2014-2016
Global Academy of Technology	Assistant Professor	Nov 2021 – Till Date

Research Publication

	International	National
Journal	10	-
Conference Publication	8	-