USE OF JAROSITE AS PART REPLACEMENT OF FINE AGGREGATES IN CONCRETE AND ITS EFFECTS ON DURABILITY

Ph.D. THESIS

by

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This thesis is submitted

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This thesis is dedicated to

My Parents

DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **"Use of Jarosite as Part Replacement of Fine Aggregates in Concrete and its effects on Durability"** in fulfillment of the requirements of the degree of Doctor of Philosophy and submitted to the Malaviya National Institute of Technology, Jaipur is an authentic record of my own work carried out at Department of Civil Engineering during a period from July, 2009 to May, 2015 under the supervision of Dr. R.C.Gupta, Professor, Civil Engineering, MNIT Jaipur.

The results contained in this thesis have not been submitted, in part or full, to any other University or Institute for the award of any degree or diploma.

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CERTIFICATE

This is to certify that the thesis entitled**, “Use of Jarosite as Part Replacement of Fine Aggregates in Concrete and its effects on Durability”** being submitted by Priyansha Mehra to the Malaviya National Institute of Technology Jaipur, for the award of the degree of Doctor of Philosophy is a bonafide record of research work carried out by her under my supervision and guidance. The thesis work, in my opinion, has reached the requisite standard fulfilling the requirement for the degree of Doctor of Philosophy.

The results contained in this thesis have not been submitted, in part or full, to any other University or Institute for the award of any degree or diploma.

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DECLARATION CERTIFICATE

I **PRIYANSHA MEHRA** declare that this thesis titled **USE OF JAROSITE AS PART REPLACEMENT OF FINE AGGREGATES IN CONCRETE AND ITS EFFECTS ON DURABILITY.** And the work presented in it is my own. The work has been carried out under the supervision of **Dr. R.C.GUPTA.**

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ABSTRACT

Industrial wastes need to be reused/reutilized in sustainable manner. Also, concrete industry demands some alternative products to be added in feasible manner. In this light, byproduct Jarosite has been incorporated in concrete. Jarosite is an industrial by product from Zinc Manufacturing industry obtained through hydrometallurgical process from its sulphide ore. It has been tried to incorporate jarosite in concrete as sand replacement. Different concrete mixtures have been prepared for three water-cement ratios (0.40, 0.45 and 0.50) and 5 jarosite replacement levels (0, 5, 10, 15, 20 and 25%). Also, Cement has been partially replaced (25%) by fly ash in all the concrete mixtures for II series of mix design.

A series of laboratory investigations were undertaken to evaluate the performance of concrete mixtures incorporating jarosite. The effect of jarosite on the mechanical properties (Compressive and flexural strength) and durability (water permeability in terms of absorption, sorptivity and diffusion, resistance to abrasion and carbonation) has been investigated. Also, Durability parameters like chloride ion diffusion, chloride ion penetration and corrosion in reinforcement of jarosite concrete were determined. The influence of jarosite in concrete against aggressive environments and agents i.e. sulphate attack has also been studied. Keeping the environmental suitability of concrete in mind and to address the innocuous effect of heavy metals present in jarosite on concrete, toxicity leaching characteristic potential test has been performed on raw jarosite and concrete samples.

In series I (without fly ash), reducing strength (compressive and flexural) has been observed with increasing sand replacement. However in Series II (with fly ash), when compared to the control mixes, encouraging results were obtained in the tests to determine the mechanical properties of the concrete with jarosite. Compressive strength of concrete in Series II at all ages (3, 7, 28 and 90 days) increased with increasing jarosite content. Similar trend has been followed in flexural strength of concrete.

The other important aspect of concrete i.e. durability for series II has been revealed as satisfactory. The resistance to abrasion in concrete has been encouraging for jarosite concrete (with and without fly ash). However, the depth of wear of all the concrete samples without fly ash found to be more than control samples. The resistance to abrasion was more for concrete samples with fly ash. The depth of wear in all concrete mixtures of Series I and II (except sample of Series I with w/c 0.45 and sand replacement 25%) falls below limits prescribed in Standards.

Concrete Mixtures in Series I have higher water permeability with high jarosite content. Water penetration in concrete with fly ash with maximum sand replacement has reduction of 25%. Moreover, other water permeability parameters i.e. sorptivity (absorption through capillary action) and absorption in jarosite concrete (Series II) has been reported appreciable. The water sorption capacity of concrete seems to be reduced with time duration.

In series II, the chloride ion diffusion in concrete and corrosion of reinforcement in jarosite added concrete has been less than control mixtures. The chloride ion penetration of concrete mixtures with fly ash after 28 and 56 days, observed to be lower as compared to control specimen.

Also, concrete mixtures with fly ash have lower carbonation and carbonation co-efficient compared with concrete samples without fly ash. Sulphate Attack has on concrete specimen after 28 and 56 days immersion in magnesium sulphate been determined in two ways (Weight and compressive strength). Gradual increase in weight and loss in compressive strength of sulphate attacked concrete specimens (Series I and II) has been observed. The percentage of increase in weight of concrete specimens in series II has been recorded lower as compared to specimens in series I. Also, the attacked specimens in series II has lesser loss in strength at higher jarosite content.

The leaching of heavy metals in concrete mixtures (up to 25 % sand replacement) for both series has been observed within the permissible limits of USEPA. The satisfactory performance of mechanical and durability properties has been validated with the morphology and mineralogy study. This has been possible through SEM images and X-Ray diffraction.

Thus, addition of jarosite as partial sand replacement in concrete (along with fly ash as mineral admixture) upto 25% could be a new alternative feasible solution to its disposal issue.

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LIST OF ABBREVIATIONS

S NO	ABBREVIATION	FULL FORM
1	AAS	Atomic Absorption Spectrophotometer
2	ASTM	American Society of Testing Materials
3	ACI	American Concrete Institute
4	BIS	Bureau of Indian Standards
5	ITZ	Interstitial Transition Zone
6	W/C	Water Cement Ratio
7	SEM	Scanning Electron Microscopy
8	XRD	X Ray Diffraction
9	XRF	X Ray Fluorescence
10	TCLP	Toxicity characteristic leaching procedure
11	USEPA	United States Environment Protection Agency
12	Dssm	Diffusion Co-efficient
13	DIN	Deutsches Institut für Normung eV (German Institute for Standardization)
14	RILEM	Réunion Internationale des Laboratoires et Experts des Matériaux, systèmes de construction et ouvrages
15	CPC	Concrete Permanent Committee
16	CSE	Copper-Copper Sulphate Electrode
17	DFS	Dump Ferrous Slag
18	DC	Direct Current
19	TMT	Thermo Mechanically Treated
20	FA	Fine Aggregates
21	CA	Coarse Aggregates

22	ISF	Imperial Smelting Furnace
23	CaO	Calcium Oxide
24	SiO_2	Silicon Dioxide
25	Al_2O_3	Aluminium Trioxide
26	Fe_2O_3	Ferrous Oxide
27	MgO	Magnesium Oxide
28	SO_3	Sulphur Trioxide
29	K_2O	Potassium Oxide
30	TiO_2	Titanium Dioxide
31	LOI	Loss on Ignition
32	Zn	Zinc
33	Pb	Lead
34	$Fe_{(T)}$	Iron
35	Ag	Silver
36	As	Arsenic
37	Cd	Cadmium
38	Cu	Copper
39	MTPA	Metric Tons Per Annum

CHAPTER 1

INTRODUCTION

1.1 GENERAL

In last few decades, mankind has made tremendous progress in technology. This urge of progress and growth of mankind in technology had resulted into large scale industrial development. Thus, establishment of various large scale industries and factories have taken a toll.

The invention of concrete has been one of the key events in industrial evolution because of its simplicity, strength, durability and the affordability for the society. It is the third most used substance in the world after air and water (Gencel et al. 2012 & 2013, Alan et al. 2012; Anh et al. 2012). One of the greatest challenges for the concrete industry is to help in the transformation of the consumption based society to a sustainable society by helping to lower the pollution of natural environment and to prevent the exhaustion of natural resources (Thomas et al. 2013 & 2014, Pelisser et al. 2011 & 2012).

Industrial wastes are often used as aggregate in concrete production to lower their production cost (Elci, 2015). Unfortunately, the new industrial processes have also led to production of large amount of hazardous waste. Metal producing industries is one such sector where several waste materials are generated along with the main products.

In India, there are many metallic and non-metallic ore extraction industries. During extraction of metals and non-metals in factories, different by-products are produced in huge quantity. The by-products can be hazardous and non-hazardous in nature. Hazardous waste means any waste which by reason of any of its physical, chemical, reactive, toxic, flammable, explosive or corrosive characteristics causes danger or is likely to cause danger to health or environment, whether alone or when in contact with other wastes or substances (HW rules 2003, 2008). Waste products containing toxic elements and heavy metals are categorized as hazardous by-product. Jarosite is one such by product which is obtained during zinc extraction through hydrometallurgical process in zinc smelters MoEF 2003, 2008).

India is the world’s 7th largest producer of zinc (MoEF 2010). Out of four zinc smelters in country, two are situated in the state of Rajasthan (Debari Zinc Smelter, Udaipur & Chanderiya Zinc Smelter, Chittorgarh), owing to the largest reserve of zinc mines (Rajpura-Dariba, Rampura-Agucha, Sindesar Khurd and Zawar). The two different processes (hydrometallurgy and pyro metallurgy) of extracting zinc have been adopted in both the zinc smelters. Debari Zinc smelter produces zinc using hydrometallurgical process leading to release of hazardous byproduct jarosite. Approximately, 48 MTPA of zinc is produced in Debari Zinc Smelter, Rajasthan (Pappu et al. 2005). This huge amount of waste not only creating disposal problems in landfills of smelters but also, adversely affecting the environment by contaminating water, air and soil. Long term benefit could be achieved through proper reuse/recycling of jarosite in sustainable manner.

Use of industrial by–products as a raw material in concrete is becoming necessary to address sustainability of both, the concrete and the industrial growth (Tripathi et al. 2012). Keeping this need in mind, this project has focused on utilization of jarosite in concrete through partial replacement of fine aggregates. Along with this, incorporating fly ash replacing cement into the jarosite-concrete matrix has been chosen for strength and durability enhancement. Properties of fresh and hardened concrete has been examined and compared with the control mixtures.

In fresh concrete, the density and workability in terms of compaction factor test has been determined. In hardened concrete, mechanical (compressive & flexural strength) has been determined.

Nowadays, five requirements including workability, safety, durability, economy and ecology, should be put together for success in concrete industry. Durability of a material is its ability to last for a long time without any significant deterioration. A durable material helps the environment by conserving resources and reducing wastes and the environmental impacts of repair and replacement (Kalla et al. 2013). In this context, different parameters for durability has been tested and evaluated.

Water penetration in terms of sorptivity, absorption and permeability has been studied.

To check the potential for long term performance and durability of concrete against abrasive forces and freeze-thaw cycles, Abrasion resistance of Jarosite concrete need to be determined (Atis 2003).

Carbonation is one of the many important factors that determine the service life of a concrete structure (Jiang et al. 2000). Depth of concrete, carbonation has been measured using accelerated test method.

Chloride ions are the most common and aggressive agent and are considered to be the major cause of premature rebar corrosion which finally leads to long term deterioration. When chloride concentration exceeds a certain threshold value, depassivation of steel takes place, leading to corrosion of reinforced bars (Guneyisi et al. 2009, Dellinghausen et al. 2012). Chloride diffusivity, Chloride Ion Penetration and Resistance to corrosion for reinforcement in jarosite concrete has been determined and extensively studied & analyzed.

Sulfate attack on concrete leads to the conversion of cement hydration products to ettringite, gypsum, and other possible phase changes leading to gradual but severe damage to concrete structures (Zhang et al. 2013). Also, sulfuric acid in groundwater, chemical waste, or generated from the oxidation of sulfur bearing compounds (e.g. pyrite) in backfill can attack substructure concrete members. Moreover, concrete structures in industrial zones are susceptible to deterioration due to acid rain of which sulfuric acid is a chief component (Bassuoni et al. 2007). Effect of sulphate on jarosite added concrete samples has been studied in terms of weight gain and loss in compressive strength.

To prevent the exhaustion of natural resources through use of jarosite in concrete and waste reuse, jarosite as replacement of fine aggregates in concrete and its effect on different properties (mechanical and durability) need to be studied. The study will provide feasible and sustainable solution.

1.2 RESEARCH HYPHOTHESIS

Rajasthan, India, has two zinc smelters, accumulating a huge quantity of jarosite, a byproduct of zinc manufacturing industry, every year. Jarosite being disposed in the landfills around the industry, contaminates the soil, water and air. Consequently, it affects the environment, human health and aquatic life adversely. Therefore, to address these issues recycling/reusing of jarosite is considered in this investigation. With the backdrop of the above mentioned the characteristic features namely, strength and durability obtained by concrete on addition of jarosite has been studied. Thus, it is aimed to reduce the aforesaid possible environmental and ecological issues. Moreover, the outcome of this investigation would introduce and validate a new composition to enhance the properties of concrete, a basic building material in construction.

1.3 OBJECTIVES OF THE STUDY

Addressing the environmental issue of disposal for jarosite (industrial waste product) has been the key of the present study. Previous studies on reuse of jarosite in various ways need to be discussed and scope for solving the scarcity problem of construction material has to be aimed. In this context, jarosite as partial replacement of fine aggregates in concrete has been used and further, certain below mentioned objectives need to be fulfilled:

a. To prepare concrete mixture with jarosite as filler in order to attain sustainability.
b. To compare different properties of concrete with respect to content of jarosite and water/cement ratio.
c. To determine the workability and density of freshly mixed concrete
d. To evaluate the mechanical properties (Compressive & Flexural strength) of jarosite added concrete and fly ash-jarosite concrete.
e. To test the water permeability of jarosite concrete (with and without fly ash) by opting the different phenomenon of penetration (Water penetration as per DIN 1048, water sorptivity and water absorption).
f. To find the resistance to abrasion for jarosite concrete in terms of wear and depth of carbonation in concrete.
g. To predict chloride ion diffusion, chloride ion penetration and corrosion of reinforcement in concrete as important durability and serviceability criteria.
h. To study the influence of jarosite in concrete against aggressive environments and agents i.e. sulphate attack.

i. Owing to the hazardous nature of jarosite, Leaching Potentials of heavy metals in concrete has to be checked for environment suitability.
j. Microstructure and chemical composition of jarosite added concrete has to be studied and analyzed in evident support to various results obtained for properties of concrete.

1.4 ORGANISATION OF THESIS

The thesis has been comprised for five chapters.

Chapter one gives a basic introduction of origin of research work. Environmental significance for use of jarosite in concrete has been discussed.

Chapter two describes the byproduct “jarosite” explicitly and its formation. Further, past studies on usage of jarosite has been revealed.

Chapter three discusses the experimental program. It includes procurement of materials, preparation of concrete samples and testing of concrete for determining different properties.

Chapter four presents all the results of experiments performed, in graphical and tabular form. The results have been understood, analyzed in order to predict the behavior of jarosite added concrete in reference to control mixtures.

Finally, Chapter five concludes the findings and outcomes of the research. Moreover, recommendations for carrying out extensive research on the same topic with more advancement have been proposed.

References and bibliography, which have been read and referenced throughout the thesis work, has been added up in the last.

CHAPTER 2

JAROSITE: CHARACTERISTICS AND PAST STUDIES

Introduction explained the need for reuse/recycling jarosite in Concrete. Objectives of research and organization of thesis has also, been discussed in previous chapter. In this section, the formation of jarosite, its characteristics and past studies regarding its utility in different ways has been discussed.

2.1 JAROSITE AND ITS CHARACTERISTICS

Jarosite is silty clay loam in texture having 88.6% silt sized and 10.9% clay sized particles. The Jarosite is non-uniform in structure and shape, hollow shaped and some of them are cenosphere in nature (Pappu et al. 2006). Figure 2.1 shows the yellow colored powdered jarosite.

Figure 2.1 Jarosite from Zinc Smelter, Debari Udaipur, Rajasthan

2.2 EXTRACTION PROCESS OF ZINC AND JAROSITE (Through personal communication to Mr B.K.Singh)

The extraction of zinc from zinc ore through hydrometallurgical process is done in 3 stages. The stages are as follows:

1. Roasting
2. Leaching and purification
3. Electrolysis

2.2.1 Roasting

Zinc Sulphide concentrate ore is fed to the fluo-solid roaster at 950°C. As a result, calcine (which is mainly zinc oxide) and sulphur oxide is produced.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

During the roasting process, entire iron present in the zinc concentrate combines with the zinc oxide and forms zinc ferrite.

$$ZnO + Fe_2O_3 \rightarrow ZnO.\ Fe_2O_3$$

2.2.2 Leaching and Purification

To extract zinc from the solution, the roasted product Calcine is leached in spent electrolyte which is rich in sulphuric acid and constituents. The zinc oxide and other metallic impurities present in the calcine are leached into solution but zinc ferrite did not decomposed. Then, the pH of leached slurry is increased to 4.7-4.9 by adding excess calcine and discharging into thickener for solid-liquid separation. The impure zinc sulphate solution is obtained, which is sent for purification.

In the process of purification, impurities like copper, cadmium, nickel, cobalt, arsenic, germanium, titanium and antimony are removed. The purified solution is then sent to Zinc electrolysis plant. The residue containing zinc ferrite which does not get dissolve at this stage is further treated. The residue is treated in a process called conversion to recover zinc from zinc ferrite and precipitate iron as jarosite.

2.2.3 Zinc Electrolysis

The purified zinc sulphate electrolyte is mixed with spent electrolyte and electrolyzed using aluminium cathode and lead anode. The zinc deposited on cathode is stripped once in 24 hours and melted in an induction furnace to convert it to saleable ingots.

2.2.4 The Conversion Process

Zinc ferrite is converted into ammonium jarosite at 95° C and at a pH that is kept constant either at 1.7 or 1.95. The rate of precipitation of ferric ion as ammonium jarosite from acid zinc sulphate solution near 100°C increased with (Phipps and Hutchison, 1977)

Increasing concentration of ammonium ion

Decreasing concentration of acid

Inreasing surface area of jarosite particles present.

In the conversion, the iron in the ferrite form is leached with spent electrolyte, as a result zinc ferrite is broken into Zn and Fe. Zn goes into the solution; whereas the leached iron gets precipitated as jarosite.

The leaching reaction in conversion is as follows:

$$ZnO.Fe_2O_3 + 4H_2SO_4 = ZnSO_4 + Fe_2(SO_4)_3 + 4H_2O$$

The jarosite precipitate happens as this reaction

$$3Fe_2(SO_4)_3 + (NH_4)_2SO_4 + 12H_2O = 2\ (NH_4)[Fe3(SO_4)_4(OH)_{12}] + 6H_2SO_4$$

The jarosite slurry is then pumped to drum filters operating under vacuum where the jarosite cake separated on the filter is washed with water to reduce the water soluble Zinc.

2.3 REVIEW OF LITERATURE

Jarosite reuse/utilization had initial experiments reported not before two decades. Past studies indicate various researches on using jarosite as a raw material for developing different products.

2.3.1 Different Uses of Jarosite

Mymrin and Vaamonde, 1999 presented the first laboratory results confirming the possibility of using these jarosite waste together with other industrial wastes; such as Dump Ferrous slag, liquid activator etc. Addition of 4% CaO or Portland cement has further enhanced the strength. Later, aluminium surface cleaning waste was also used along with industrial wastes like DFS and activator in jarosite and recommended to be used as substitute of natural crushed stones, gravel and sand applicable as bases or sub-bases of roads, airfields (Mymrin et al. 2005). Also bricks, tiles and similar products have been developed using jarosite (Mymrin et al. 1999, 2004). The strength development in the newly developed materials was mainly attributed to formation of amorphous gel in the pores. Moreover, the crystalline hydrated form of other compounds were held responsible for enhanced strength. Along with consideration to economic factors, these applications are very easy to use and no new residues are generated (Mymrin and Vaamonde, 1999).

In the same decade, studies have been made for an alternative reuse in production of glass and glass ceramics materials. The properties of these glass and glass-ceramics favored the commercial exploitation of the products in the building industry, in the form of paving tiles wall covering panels, glass fibers for insulation and coloring pigments for ceramics. (Pelino 2000).

During these years, solidification/stabilization technique developed as one of the waste treatment/management technique. Stabilization is a process of converting a toxic waste to a physically and chemically more stable form. It involves chemical interactions between waste and the binding agent. The method has been adopted as an application of model involving coupled process of diffusion and precipitation at the interface of two material layers) potential use to form a self-sealing layer in jarosite/fly ash co-disposal sites (Ding 1998, 2001). The solidification can be achieved by (a) chemical means (e.g. formation of precipitates, reactions with cement, etc.); (b) isolation in a protective binding agent (e.g. imbedding in polymers, thermoplastic materials, etc.); and (c) physical means (e.g. evaporation of water from aqueous wastes or sludge, sorption onto an appropriate solid adsorbent, vitrification, etc. The combined effect of s/s prevents pollutants from migrating into the environment by making the toxic contaminants physically immobile and/or chemical bonding to the binders. The containment of the waste by s/s improved its handling characteristics and lowered the leaching rate by reducing the surface area of the solid (Yousuf et al. 1995). Using the same technique, Jarosite/alunite (J/A) precipitate along with cement was investigated as an alternative for the final disposal of sewage sludge from urban wastewater treatment plants (Cheilas et al. 2007).

Also, research carried by Pappu et al. 2006, confirmed that fly ash has got huge potential for immobilization of hazardous metals present in jarosite and its usefulness in developing non-hazardous materials for construction purposes. Bricks have been produced using the same technique combining jarosite, coal combustion residues and clay in different proportions. Jarosite mixed with fly ash and clay to prepare a homogenous mortar has been tested for different properties like physio chemical, engineering, mineralogical and micro structural studies. The jarosite product has attained higher compressive strength on increasing jarosite and clay ratio. The results of study also revealed that different physical properties (density and water absorption) of jarosite bricks has also been examined and found appreciable. Moreover, this process inhibited the transport of pollutant elements into the surrounding environment and improved the physical characteristics, thus reducing the transport and leaching of contaminants/toxic metals (Pappu et al. 2006, 2006*).

Ochereous mine water along with jarosite residue had been mixed to form controlled low strength material. Investigating the different properties of prepared material approved the suitability for sub surface applications (Bouzalakos et al. 2007).

The application of model to industrial layered acidic jarosite/alkaline fly ash deposition suggests that there is a potential benefit to layered disposal of these two chemically contrasting wastes. By making use of neutralization, isolation (sealing layer formation due to pores filling by precipitates), and immobilization (reduce mobility of chemical constituents due to precipitation) chemical reactions, such wastes can be disposed of successfully in an environmentally acceptable manner (Ding et al. 2002).

2.3.2 Use of other zinc by products in Concrete

But till date no experimental work regarding utilization of jarosite in concrete was reported. However, researchers have been investigating the possibilities for using other byproducts (containing zinc and lead) of zinc manufacturing industries in mortar and concrete. ISF slag (Imperial smelting furnace slag) produced as secondary material during pyro metallurgical operation of zinc production has been added as partial replacement of fine aggregates in concrete. Previous studies have revealed that use of ISF slag in concrete and mortar has indicated positive results (Morrison et al. 2003, Tripathi et al. 2012, Tripathi and Chaudhary 2016). The incorporation of ISF slag as partial replacement of sand up to 70 percent supports durability and sustainability of concrete. The other by-products like coal bottom ash from coal fired thermal power plants has been utilized as filler in concrete. (Agrawal and Siddique, 2014; Singh and Siddique, 2015, 2016).

CHAPTER 3

MATERIALS AND METHODS

The experimental process is three-step process, including procurement of materials, preparation of concrete samples and testing of concrete for determining different properties. Procurement of materials include collection of different raw materials for molding concrete into samples to be tested for different mechanical and durability properties of hardened concrete. The experimental results have been discussed in chapter 4.

3.1 MATERIALS

3.1.1 Cement

Ordinary Portland Cement Grade 53 procured from ULTRATECH INDUSTRIES, conforming the guidelines of IS 12269-1987 has been used for preparing the concrete mixtures. The physical properties of cement have been tested and given in table 3.1. .

Table 3.1 Physical Properties of cement

Properties		Values	Standards
Consistency (%)		31	IS 4031 part 4-1988
Setting time (minutes)	Initial time	35	IS 4031 part 5-1988
	Final time	310	
Specific Gravity		3.14	IS 1727-1967
Fineness (%)		2	IS 4031 part 1-1996
Compressive Strength (N/mm^2)	3 days	25	IS 4031 part 5-1988
	7 days	39	
	28 days	57	

The chemical analysis and composition of cement has been tabulated in Table 3.2 and 3.3 respectively. SEM micrograph of cement has been presented in Figure 3.1. The Scale of micrograph is 2 µm and magnification 4kX.

Table 3.2 Chemical Analysis of Cement

S No	Chemical Requirements	Test Value	Value as Per IS	
			Maximum	Minimum
1	$\frac{CaO-0.7SO_3}{2.8\ SiO_2+1.2Al_2O_3 + 0.65\ Fe_2O_3}$	0.84	1.02	0.66
2	Al_2O_3 / Fe_2O_3	1.30		0.66
3	Insoluble Residue (% by mass)	2.56	4	-
4	Magnesia (% by mass)	1.14	6	-
5	Sulphuric Anhydride (% by mass)	2.03	3.50	-
6	Total Loss on Ignition (% by mass)	2.69	5.00	-
7	Total Chlorides (% by mass)	0.020	0.10	-

Source: Electronic Communication From Ultratech Cement

Table 3.3 Chemical Composition of Cement

Compounds	% by Mass
CaO	64.02
SiO_2	20.15
Al_2O_3	5.69
Fe_2O_3	0.60
MgO	1.17
SO_3	3.49
Na_2O_3	0.15
K_2O	0.79
TiO_2	0.32
LOI	1.78

Source: Electronic Communication From Ultratech Cement.

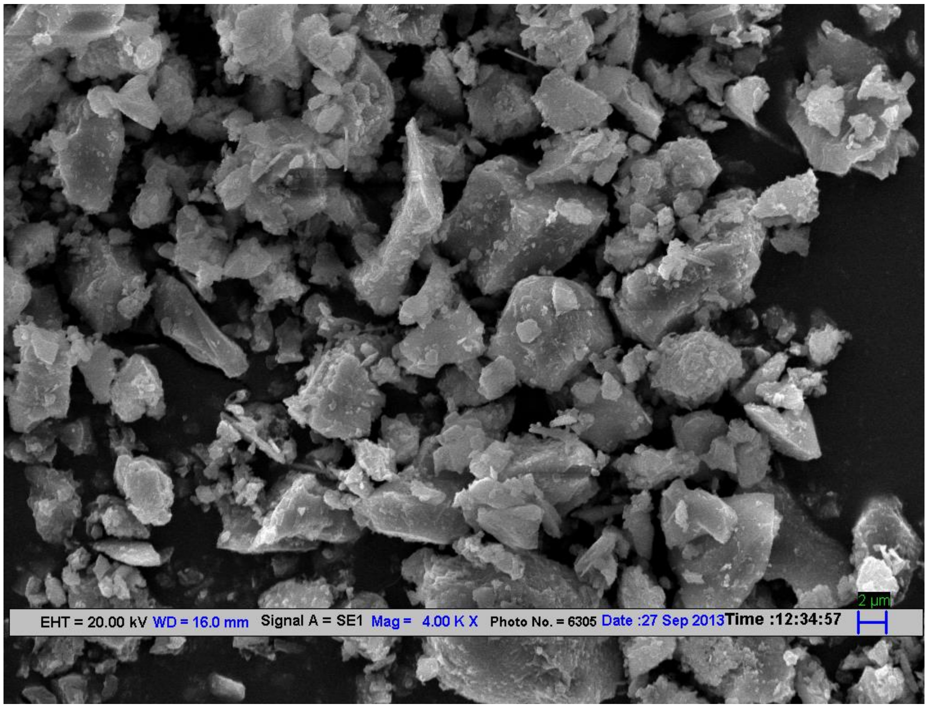


Figure 3.1 SEM Image of Cement

3.1.2 Water and Super Plasticizer

Natural potable water as per IS 456-2000 along with Superplasticizer based on polycarboxylic ether conforming to ASTM type-F has been used in the complete research work. The properties of superplasticizer are as mentioned in Table 3.4.

Table 3.4 Properties of Plasticizer

Properties	Values
Aspect	Light brown liquid
Chloride ion content	< 0.2 %
pH	> 6
Relative Density	1.10 ± 0.01 at 25° C
Solid Content	>40% by weight

Source: (www.basf-cc.co.in)

3.1.3 Jarosite

Jarosite used for the present work has been supplied by Sterlite Industries formerly Hindustan Zinc Limited, Debari, Udaipur. Addition rate of jarosite has been kept 0-25% by mass of fine aggregates in the concrete mixture.

Debari Zinc Smelter produces Ammonium type Jarosite. The chrome yellow coloured jarosite possesses silty clay loam texture having 88.6% silt sized and 10.9% clay sized particles. The Jarosite has non-uniform structure and shape, hollow shaped and some of them being cenosphere in nature. The calculated specific gravity occurred to be 2.8. The chemical composition and physical properties of jarosite have been given in table 3.5 and 3.6 respectively.

Table 3.5 Chemical Composition of Jarosite

Element	Percentage	Element	Percentage
Zn	2 - 4%	MgO	0.65-1.0%
Pb	2 – 5.8%	Mn_2O_3	0.4-0.5%
$Fe_{(T)}$	24-28%	CaO	7-10%
Ag	150-300 ppm	SiO_2	9-11%
As	400 – 600 ppm	Acid Insoluble	7-9%
Cd	0.02-0.05%	$S_{(T)}$	12-15%
Cu	0.06-0.13%	Al_2O_3	1.4-1.6%

Table 3.6 Physical Properties of Jarosite

Property	Value	Property	Value
% Of Sand Size	10.5	Specific Gravity	1.86
% Of Silt Size	78.6	Optimum Moisture Content (%)	34
% Of Clay Size	10.9	Maximum Dry density (g/cc)	1.30
Liquid Limit (%)	24.8	Cohesion (kPa)	12.5
Plastic Limit (%)	21.7	Angle of Internal friction (deg)	300
Plasticity Index	3.1	pH	6.83

Source (Table 3.5 & 3.6): (Personal Communication Mr.B.K.Singh, HZL Chanderiya)

The XRD (Figure 3.2) and XRF (X-Ray Fluorescence) studies on Jarosite sample were performed at Concrete Technology Laboratory, University of Dundee, U.K. (Table 3.7) for the reassurance of the data provided by Hindustan Zinc Ltd.; which confirm the values of the latter.

Table 3.7 Oxide Composition of Jarosite Sample

S no	Element	%	S no	Element	%
1	Fe2O3	37.549	12	Cu	0.229
2	SO3	29.348	13	TiO2	0.165
3	SiO2	13.018	14	MnO	0.115
4	Pb	3.735	15	P2O5	0.092
5	Zn	3.679	16	Cl	0.050
6	Al2O3	3.206	17	Cr	0.024
7	CaO	2.808	18	Ag	0.023
8	Cd	2.407	19	Tl	0.015
9	K2O	0.625	20	Sr	0.010
10	Na2O	0.559	21	V	0.009
11	MgO	0.302	22	Am	0.009

Source: Concrete Technology Unit, University of Dundee, United Kingdom

The SEM image of Jarosite has been presented in figure 3.3. The scale of micrograph is 1 micron with magnification of 4Kx. The image depicts angular shape and non-uniform structure of Jarosite.

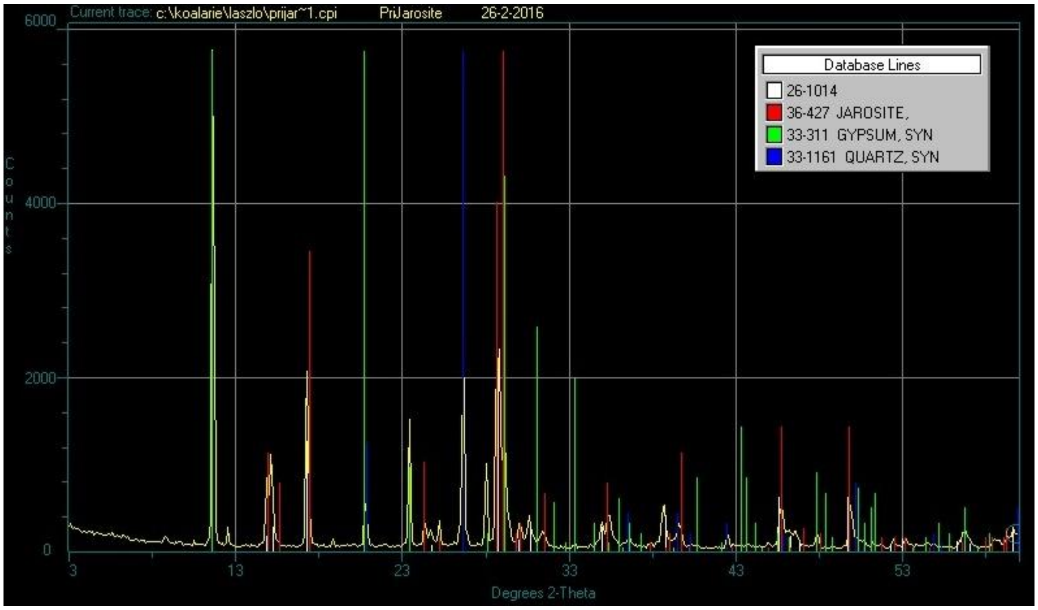


Figure 3.2 XRD of Jarosite

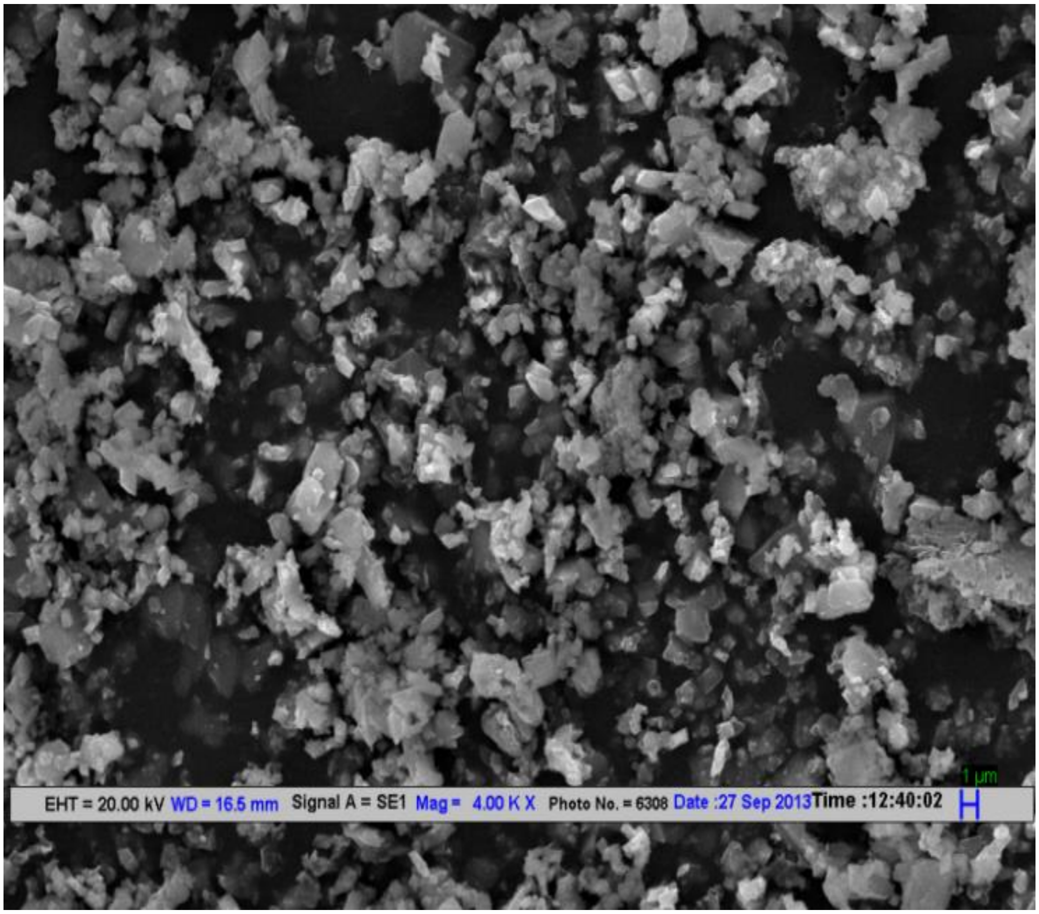


Figure 3.3 SEM image of Jarosite

3.1.4 Fly ash

Fly Ash ‘Class C’ has been procured from Kota Super Thermal Power Station, Kota, Rajasthan. The specific gravity and fineness of fly ash has been calculated as 2.3 and 12% respectively. Table 3.8 shows the chemical composition of Fly Ash.

Table 3.8 Chemical Composition of Fly Ash

Compounds	% by Mass	Compounds	% by Mass
CaO	15.9	SO_3	4.6
SiO_2	47	Na_2O	2.9
Al_2O_3	10	K_2O	2
Fe_2O_3	9.8	TiO_2	0.7
MgO	2.7	LOI	2.1

Figure 3.4 demonstrates the graph representing particle size distribution of Jarosite, fly ash and fine aggregates. Jarosite and fly ash seems to have similar particle size whereas fine aggregates are coarser than the other two.

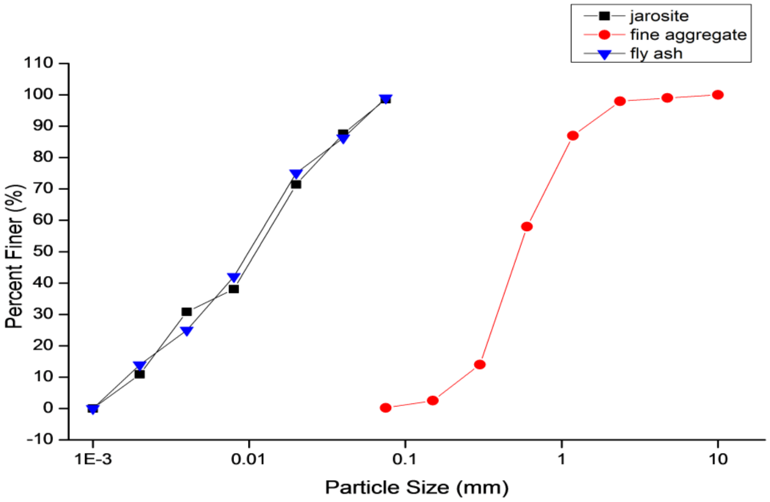


Figure 3.4 Particle Size of fly ash, fine aggregates and jarosite

SEM Micrograph of fly ash is shown in Figure 3.5. Fly Ash possess spherical and hollow shape and structure.

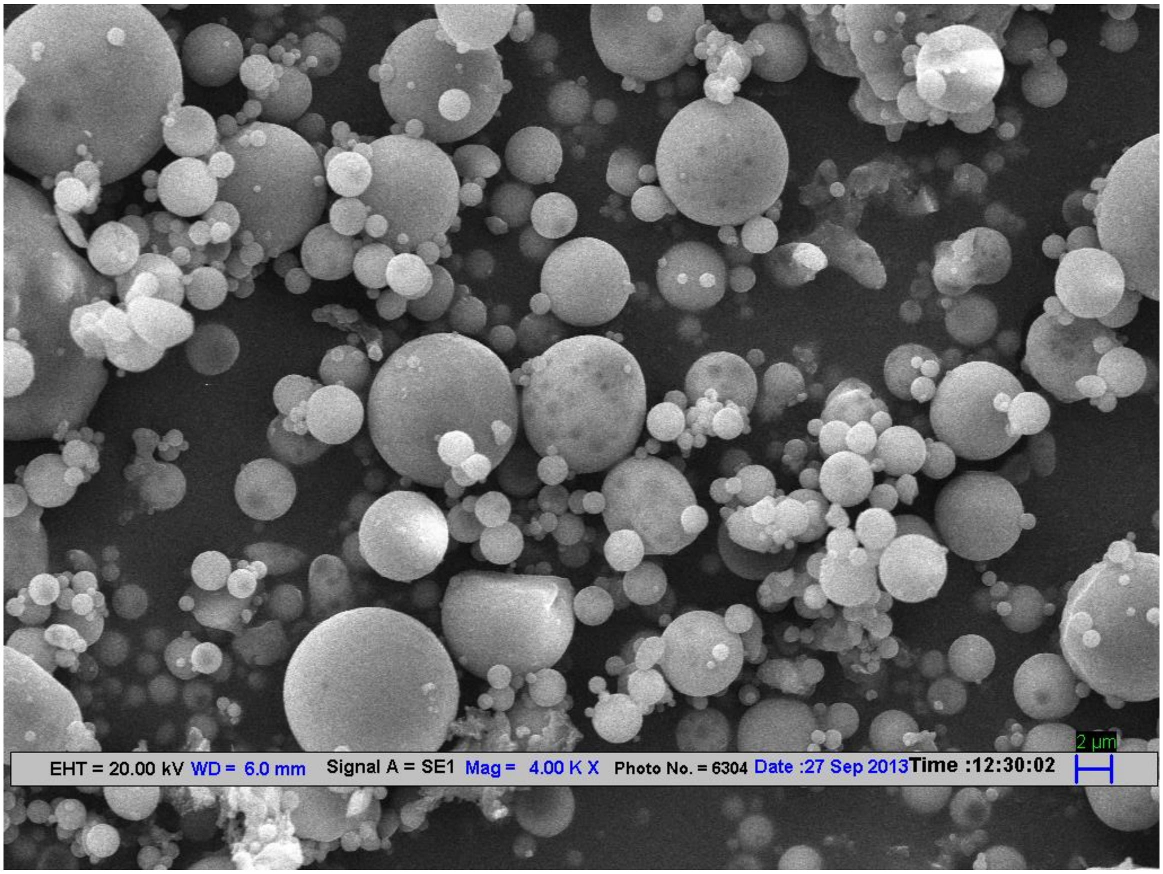


Figure 3.5 SEM Image of Fly Ash

3.1.5 Fine Aggregate & Coarse Aggregate (10 mm & 20 mm)

The aggregates used in this study has been procured locally and tested. Fine Aggregates conforming to Zone II as per IS: 383-1970, locally available river sand has been used as fine aggregate for the test process. The physical properties of fine aggregates are determined and represented in Table 3.9.

The grading for a given maximum-size coarse aggregate can be varied over a moderate range without appreciable effect on cement and water requirement of a mixture if the proportion of fine aggregate to total aggregate produces concrete of good workability. The maximum size of coarse aggregate used in concrete has a bearing on the economy of concrete. Usually more water and cement is required for small-size aggregates than for large sizes, due to an increase in total aggregate surface area. Coarse aggregate of 10mm and 20 mm aggregates has been used for the concrete mixes.

Table 3.9 Properties of aggregates

Properties	FA	CA (10 mm)	CA (20 mm)	Jarosite
Specific Gravity	2.65	2.66	2.66	2.8
Water Absorption	0.28%	0.33%	0.32%	1.4%
Fineness Modulus	2.6	2.9	3.2	-
Bulk Density, kg/m^3	1668	1463	1452	975
Soundness	4.3%	5.6%	5.2%	-

3.2 MIX DESIGN

IS 10262-1982 has been used for designing control concrete mixtures (Grade M25). In India, general construction is carried out with M25. Therefore, we tried to solve the problem of recycling industrial waste (Jarosite) using local grade of concrete. Water/cement ratio 0.45 has been adopted and quantities of other raw materials calculated as per aforementioned standard and the mixtures with w/c 0.40 & 0.50 have been proportioned keeping cement constant (w/c 0.40 & 0.50). The proportions for desired grade of concrete have been tabulated in Table 3.10.

Table 3.10 Ratios of mix design

Water	Cement	Sand	10 mm	20 mm	Plasticizer
17.1 l	38 kg	71.300 kg	58.2 kg	58.2 kg	228 ml
0.45	1	1.876	1.532	1.532	0.6%

Initially, design series comprised of concrete mixtures with varying percentages of jarosite (0, 5, 10, 15, 20, and 25%) as part replacement of fine aggregates. The limits of Jarosite has been restricted up to 25%, as above levels of jarosite results into honeycombing of concrete. Trials for the designed mixtures has been performed and observed that non- homogenous and non-workable mixtures resulted at lower w/c 0.40 & 0.45 and higher jarosite content (15, 20 and 25%). More water absorption by powdered jarosite during mixing could be reason for improper mixtures. Also, proper compaction through vibrations did not improve the non-homogeneity and workability of the concrete mixtures. After various trials with different plasticizers to make mixture, super plasticizer based on polycarboxylic ether proved efficient enough to enhance water content in the mixtures. Thus, sufficient dosage of plasticizers has been added in all the mixtures for optimum results.

Further, 3 days compressive strength for trial concrete mixtures has been determined. The results predicted lower strength with increasing jarosite content. Thus, research objective for achieving durable and strong jarosite added concrete, led to designing of second series (fly ash partially replaced 25% of cement along with varying percentages of jarosite as in series I).

The proportions of different materials for concrete mixtures in both series have been provided in table 3.11 & 3.12 below respectively.

Table 3.11 Concrete Mix Design (Series I)

Sample	Jarosite (%)	Water/ Cement ratio	Water (Kg)	Cement (Kg)	FA (Kg)	CA 10 mm (Kg)	CA 20 mm (Kg)	Jarosite (Kg)	Plasticizer (gm)
J1	0	0.40	15.2	38	71.30	58.2	58.2	0	380
J2	5	0.40	15.2	38	67.73	58.2	58.2	3.57	456
J3	10	0.40	15.2	38	64.17	58.2	58.2	7.13	532
J4	15	0.40	15.2	38	60.61	58.2	58.2	10.69	608
J5	20	0.40	15.2	38	57.04	58.2	58.2	14.26	684
J6	25	0.40	15.2	38	53.48	58.2	58.2	17.83	760
J7	0	0.45	17.1	38	71.3	58.2	58.2	0	228
J8	5	0.45	17.1	38	67.74	58.2	58.2	3.57	342
J9	10	0.45	17.1	38	64.17	58.2	58.2	7.13	418
J10	15	0.45	17.1	38	60.61	58.2	58.2	10.70	494
J11	20	0.45	17.1	38	57.04	58.2	58.2	14.26	570
J12	25	0.45	17.1	38	53.48	58.2	58.2	17.83	646
J13	0	0.50	19.0	38	71.30	58.2	58.2	0	152
J14	5	0.50	19.0	38	67.74	58.2	58.2	3.57	190
J15	10	0.50	19.0	38	64.17	58.2	58.2	7.13	228
J16	15	0.50	19.0	38	60.61	58.2	58.2	10.70	304
J17	20	0.50	19.0	38	57.04	58.2	58.2	14.26	380
J18	25	0.50	19.0	38	53.48	58.2	58.2	17.83	418

Abbreviations FA: Fine Aggregates, CA: Coarse aggregates

Table 3.12 Concrete Mix Design (Series II)

Series II	Jarosite (%)	Water/ Cement ratio	Water (Kg)	Cement (Kg)	Fly Ash (Kg)	Fine Aggregate (Kg)	10 mm (Kg)	20 mm (Kg)	Jarosite (Kg)	Super Plasticizer (gm)
F1	0	0.40	15.2	28.50	9.50	71.30	58.2	58.2	0	304
F2	5	0.40	15.2	28.50	9.50	67.73	58.2	58.2	3.56	342
F3	10	0.40	15.2	28.50	9.50	64.17	58.2	58.2	7.13	418
F4	15	0.40	15.2	28.50	9.50	60.60	58.2	58.2	10.69	494
F5	20	0.40	15.2	28.50	9.50	57.04	58.2	58.2	14.26	570
F6	25	0.40	15.2	28.50	9.50	53.48	58.2	58.2	17.82	646
F7	0	0.45	17.1	28.50	9.50	71.30	58.2	58.2	0	152
F8	5	0.45	17.1	28.50	9.50	67.73	58.2	58.2	3.56	228
F9	10	0.45	17.1	28.50	9.50	64.17	58.2	58.2	7.13	304
F10	15	0.45	17.1	28.50	9.50	60.60	58.2	58.2	10.69	380
F11	20	0.45	17.1	28.50	9.50	57.04	58.2	58.2	14.26	494
F12	25	0.45	17.1	28.50	9.50	53.47	58.2	58.2	17.82	570
F13	0	0.50	19.0	28.50	9.50	71.30	58.2	58.2	0	0
F14	5	0.50	19.0	28.50	9.50	67.73	58.2	58.2	3.56	114
F15	10	0.50	19.0	28.50	9.50	64.17	58.2	58.2	7.13	190
F16	15	0.50	19.0	28.50	9.50	60.60	58.2	58.2	10.69	228
F17	20	0.50	19.0	28.50	9.50	57.04	58.2	58.2	14.26	304
F18	25	0.50	19.0	28.50	9.50	53.47	58.2	58.2	17.82	380

3.3 PREPARATION OF CONCRETE MIXTURES

All the raw materials has been weighed for the desired quantities and fed in to the pan mixer (shown in figure 3.6) following the sequence (First coarse aggregates, fine aggregates, Cement and water mixed with admixture). As discussed earlier, powdered jarosite made concrete mixture harsh and non-workable. Therefore, jarosite slurry (half quantity of water added to jarosite) instead of powdered jarosite, has been fed to mixer. Mixing time of the concrete mixtures in mixer has been kept 10 minutes owing to the use of polycarboxylic based hyper plasticizer. Filling of moulds has been done by vibrating the prepared concrete mixtures into 3 layers. 21 cubes of size 100X100X100mm, 6 cubes of size 150X150X150 mm, 3 corrosion prism of size 250X210X130 mm, 6 beams of size 100X100X500 mm and 3 slabs sized 100X300X500 mm has been casted. The concrete filled moulds have been kept for 24 hours for setting, unmolded and cured in water till the time of testing or 28 days.

Figure 3.6 Pan Mixer

Figure 3.7 Casting of 100 × 100 × 100 mm Cubes and 100 × 100× 500 mm Beams.

3.4 TESTING OF CONCRETE

Table 3.13 enlists various tests which have been conducted just after the mixing and soon after the curing period.

Table 3.13 List of Concrete Tests

No.	Test	Standards and Codes
1	Compacting Factor Test & Density	IS 1199 -1959
2	Compressive Strength Test	IS 516 – 1959
3	Flexural Strength Test	IS 516 – 1959
4	Water Permeability	DIN 1048-1991
5	Water Absorption Test	ASTM C642-06
6	Water Sorptivity Test	ASTM C1585-13
6	Abrasion Test	IS 1237 – 1978
7	Carbonation Test	RILEM CPC 18
8	Corrosion Test	ASTM G109, 876, G3
9	Chloride Diffusivity Test	Steady State Condition
10	Chloride Ion Penetration	ASTM C1543-2002
11	Sulphate Attack Test	ASTM C1012 - 1989
12	Toxicity Characteristics Leaching Potential Test	USEPA 1311
13	SEM Analysis & X ray diffraction	

3.4.1 Compaction Factor and density Test

Compaction factor and density of concrete has been measured as per IS-1199-1959. The compacting factor test works on the principle of determining the degree of compaction achieved by a standard amount of work done by allowing the concrete to fall through a standard height.

The density of fresh concrete measured by weighing the cylinder filled with concrete and dividing with its volume. It is expressed in Kg/m^3.

3.4.2 Compressive and flexural strength

The strength test was performed as per IS 516-1959 to determine the compressive strength of concrete after 7-days and 28-days. This is the most common test conducted on the hardened concrete. The compressive strength has been calculated by dividing the load at failure with the cross-sectional area of the specimen.

This test was conducted as per IS 516–1959 to determine the flexural strength of the concrete after 7 days and 28 days. The concrete specimen of size 100X100x500 mm has been casted and cured.

3.4.3 Water Absorption Test

Water absorption test on concrete has been conducted according to the procedure laid in ASTM C642-06. The concrete specimen of size 100X100X100 mm has been kept in oven at 60-70° C for 72 hours. The weight of oven dried specimen has been recorded and kept in water bath for 48 hours at 20 C. the specimen after immersion has been measured. The water absorption has been calculated by following:

Water absorption (%) = (A-B)/BX100 where,

A = weight of oven dried specimen

B = weight of specimen after immersion.

The average value of three specimens has been calculated and recorded.

3.4.4 Water Sorptivity test

Sorptivity is a property which characterizes the tendency of a porous material to absorb and transmit water by capillarity. Sorptivity test has been carried on specimen size 100X100X100. The sides of concrete specimen have been sealed with wax excluding top and bottom. Specimens have been kept in a container in such a pattern that they rest on rods and water filled not more than 5 mm above the base of concrete sample. The quantity of absorbed water has been measured at time intervals of 10 mins, 30 mins, 1 hour and 2 hours.

The sorptivity has been determined by the following formula;

$i = S \text{ X } t^{0.50}$

where,

i= increase in mass in gm/mm^2 since the beginning of the test per unit of cross sectional area in contact with water, 1gm is equivalent to 1 mm^3, so that i can be expressed in mm

t = time, measured in minutes, at which mass is determined, and

S = sorptivity in mm/min$^{0.50}$.

Figure 3.8 Concrete Samples (Series I) Placed on Rods for Capillary Action

Figure 3.9 Concrete Samples (Series II) Placed On Rods for Capillary Action

3.4.5 Abrasion Test

The Tile abrasion test of the concrete cubes was conducted as per IS 1237- 1980.

The specimen was dried at room temperature for 24 hours and then weighed. The grinding path of the disc of the abrasion testing machine was evenly strewn with 20 g of the abrasive powder. The abrasive powder with rounded shaped grains, used in the experiment has been supplied by Yemberzal Industries and specifications mentioned in Annexure A. The powder with rounded shaped grains has been The specimen was then fixed in the holding device with the surface to be ground facing the disc, and loaded at the center with 300 N. Owing to the change in size of dimensions of specimens as per IS specification, the load has been doubled and calibrated. The grinding disc was then put in motion at a speed of 30 rev/min and the abrasive powder was continuously fed back on to the grinding path so that it remain uniformly distributed in a track corresponding to the width of the test piece. After every 22 revolutions, the disc was stopped, the abraded tile powder and the remainder of the abrasive powder were removed from the disc, and fresh abrasive powder in quantities of 20 g was applied each time. After every 22 revolutions the specimen was turned about its vertical axis through an angle of 90º in the clockwise direction and it was repeated 9 times thereby giving total number of revolutions of 220. The disc, the abrasive powder and the specimen was kept dry throughout the duration of the test. After the abrasion was over, the specimen was reweighed.

The average wear in thickness of the specimen was obtained by the following formula:

$$t = \frac{(W_1 - W_2) \times V_1}{W_1 \times A}$$

Where,

t = average loss in thickness in mm,

W_1= initial mass of the specimen in g,

W_2= final mass of the abraded specimen in g,

V_1= initial volume of the specimen in mm^3

A = surface area of the specimen in $mm^{2.}$

Figure 3.10 Tile Abrasion Testing Machine

3.4.6 Water Permeability

Water permeability has been determined as per the procedure laid in DIN 1048-1991 (apparatus shown in figure 3.11).

Figure 3.11 DIN 1048 Apparatus for permeability test

The basis reason of opting German standard over Indian standard (IS 3085-1965) lies in the fact the applied pressure of 0.50 MPa require water column of 50m which is not feasible. The permeability test gives a measure of the resistance of concrete against the penetration of water pressure. The 28 days cured and oven dried concrete specimen of size 150X150X150 mm has been clamped on the permeability apparatus as shown in figure 3.11. Water pressure of 0.50 N/mm^2 has been exerted on the surface of concrete specimen, acting normal to the mould filling direction. The pressure has been kept constant for three days. After three days, the specimens have been unclamped and split into two halves. Then the maximum depth of water penetration has been measured and the extent of water penetration established. The mean of the maximum depth of penetration of three specimens has been recorded.

3.4.7 Carbonation

Carbonation test was performed as per RILEM CPC-18 on concrete to measure the depth up to which the formation of $CaCO_3$ has taken place. The 28 days cured concrete samples of size 100X100X100 mm has been sliced into four equal parts of size 50X50X100 mm. the sliced has been kept in oven at 50-60° C temperature for two weeks. Epoxy paint has been coated on the longitudinal sides of slices leaving the two opposites uncoated for diffusivity of CO_2 with portandlite and C-S-H. The prepared samples have been kept in carbonation chamber where relative humidity 55-65%, carbon dioxide 5+0.5% and temperature 27± 2° C has been maintained. Observations have been taken for three samples of each mix after exposure of 7, 14, 28, 42, 56, 70, 84 and 100 days in carbonation chamber (as shown in figure 3.12).

Each specimen has been broken into two halves and pH indicator has been sprayed on both the broken faces. A standard solution of 1% phenolphthalein in 70% ethyl alcohol was used. In the noncarbonated region with pH values above 9.2, the phenolphthalein indicator turns purple-red and in the carbonated portion with pH less than 9.2, the solution remains colorless.

The average depth of carbonation has been calculated for each concrete mix at different time of exposures. Also, carbonation co-efficient has been calculated using the expression associated with Fick’s first law of diffusion

$D = Kt^{0.5}$

Where,

D = Depth of Carbonation (mm)

t = time of exposure (days)

K = Carbonation Co-efficient (mm/$\sqrt{\text{day}}$) (Monteiro et al. 2012)

Figure 3.12 Accelerated Carbonation Chamber

3.4.8 Chloride Ion Diffusivity Test

The diffusion of chloride ions in concrete has been evaluated under steady state condition. Cutting of core of diameter 60 mm and thickness 35-40 mm from 28 days cured slab using core cutting machine has been done (Figure 3.13).

Three cylindrical cores have been cut for each set of concrete mix. The upper and bottom of cores has been covered with masking tape and the sides coated with silicon sealant and packed with rubber gasket. The sealed specimens have been soaked in distilled water for 24 hours following the uncovering of upper and bottom surfaces. The apparatus set up (figure 3.14) has diffusion unit composed of two cells, in which upstream cell has been filled with 3% sodium chloride (anode), downstream filled with distilled water (cathode) and concrete core mounted between the cells.

Figure 3.13 Specimens for chloride diffusion study

The cell has been applied with potential difference of 30 V DC. The chloride concentration in upstream and downstream cell has been determined using argentometric titration.

The slope of the steady state condition can be used in Nernst–Planck equation to determine a coefficient of ion migration, in m^2/s. (Basheer et al. 2005)

$$Dmig = \frac{JRTL}{zFcE}$$

where,

Dmig = in situ migration coefficient, m^2/s

J = (V/A) X (dc/dt), (dc/dt is the steady outflow rate, mol/cm^3; V is the volume of the outer cell, cm3; and A is the average transmission area, cm^2)

T = average temperature during the test, K

L = average flow length (m),

z = valency

F = Faraday constant $9.65X10^4$ c/mol

C = concentration of the salt solution, mol/cm^3

E = applied voltage, V dc

The average chloride coefficient of three specimens has been calculated and presented.

Figure 3.14 Apparatus for measuring chloride ion diffusion

3.4.9 Chloride Ion Penetration Test

Silver nitrate spraying test was used to study the depth of chloride penetration. The test specimens (100 mm concrete cubes) after 28 days of water curing, were subjected to continuous soaking for 91 days in 4% NaCl solution. The test specimen were periodically withdrawn at 28 days from the soaking tank and tested for depth of chloride permeability. The cubes were split into two halves from the middle and the freshly split pieces were sprayed with 0.1 N silver nitrate ($AgNO_3$) solution. The $AgNO_3$ reacts with the free chloride on the concrete surface and form a white precipitate of silver chloride (AgCl). In the places where the free chlorides are absent, $AgNO_3$ reacts with hydroxide to form a brown precipitate of silver oxide (AgO).Thus, the boundary of colour change indicates the depth of chloride permeability.

The depth of chloride penetration was obtained by measuring the average depth of penetration in three samples. The formation of silver chloride (white colour) occurs only when the concentration of free chloride ion is greater than 0.15% by weight of cement.

3.4.10 Corrosion Test

The half-cell potential has been used to monitor corrosion activity in concrete specimens. The half-cell potential measurements have been carried out with reference to CSE (Copper–Copper sulphate electrode). Concrete prism of size 250X205X135 mm similar to that specified in ASTM G 109-2005, was prepared. The reservoir or ponding well of 15 mm depression made on top of each concrete specimen used for ponding with 3% sodium chloride solution.

Measurement of Corrosion requires arrangement shown in figure 3.15 and explained. Three TMT (Thermo Mechanically Treated) 12 mm diameter steel bars has been used as top and bottom reinforcing bars. In this arrangement the top one bar acts as anode and the bottom two bars acts as cathode. The ratio of 1:2 for anode: cathode bars has been made to accelerate the corrosion process. The bars of length 350 mm have been adopted in which 50 mm length of bars from each side of concrete prism will be protruding outside. Further, bars up to 70 mm length from both the corners have been double coated with epoxy based paint. Remaining length of 210 mm (350 mm-70 mmx2) in bars has exposure to corrosion.

The specimens have been subjected to alternate wetting and drying cycles. The alternate wetting and drying cycles include 3 days of ponding with 3% sodium chloride solution followed by 12 days of drying. The potential measurements have been taken at the beginning of both wetting and drying periods for all the specimens.

The open circuit potential was measured monthly after disconnecting the top and bottom bars and allowing the current to stabilize for a period of 24 hrs. High impedance voltmeter was used to measure the potential. The electrochemical potential is a measure of electron charge transfer between the steel and the cement pore water solution (Hansson 1984). Therefore, this method provides the potential difference between the steel surface and a reference electrode.

As per ASTM C 876 (ASTM 2009b), the potential difference with respect to copper-copper sulphate reference electrode can be used to predict the probability of corrosion, which is given as follows:

i. If potentials over an area are more positive than −200 mV, then there is a greater than 90% probability that no reinforcing steel corrosion is occurring in that area at the time of measurement.

ii. If potentials over an area are in the range of −200 to −350 mV, then corrosion activity of the reinforcing steel in that area is uncertain.

iii. If potentials over an area are more negative than −350 mV, then there is a greater than 90 % probability that reinforcing steel corrosion is occurring in that area at the time of measurement.

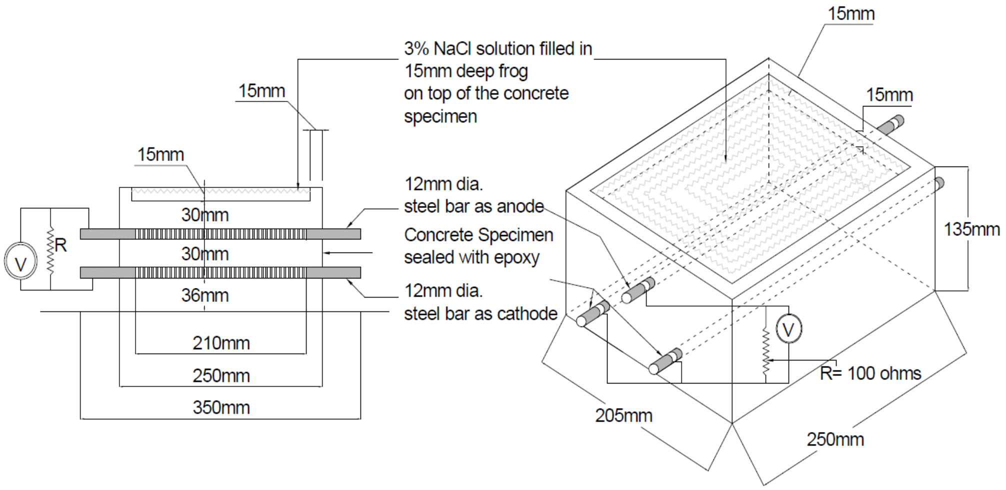


Figure 3.15 Sketch arrangement of concrete prism for corrosion.

(Source: Bhavna Tripathi PhD Thesis)

3.4.11 Toxicity Characteristic Leaching Potential Test

Use of hazardous jarosite in concrete has urged the necessity of checking the environmental suitability of concrete. The presence of toxic elements and heavy metals such as nickel chromium, cadmium and arsenic has been determined. Toxicity Characteristic Leaching Potential test (TCLP) has been conducted on raw jarosite and concrete with 25% jarosite replacement. The crushed and mortar powder has been collected out of concrete to prepare the extract as per Method 1311 described by United States Environmental Protection Agency (USEPA 1992). Atomic Absorption Spectrophotometer (AAS) has been used to determine the amount of different heavy metals and toxic elements. (Environmental Laboratory, HZL Chanderiya, Chittorgarh, Rajasthan)

3.4.12 Sulphate Attack

Sulphate attack can be defined as damage to concrete caused as consequences of chemical reactions involving the sulfate ion, recognizing that all reactions have physical consequences (A.M.Neville, 2004). The resistance to sulphate attack was studied by immersing the 28 and 56 days cured standard cube specimens (100 × 100 × 100 mm) in a solution containing 7.5% magnesium sulphate. The concentration of the solution was maintained throughout the period by changing the solution periodically. The change in weight during the period of 28 and 56 days was determined (ASTM C 1012-89). Also, loss in compressive strength of sulphate attack specimen has been measured after 56 days of immersion in $MgSO_4$ solution.

3.4.13 Mineralogical & Morphological Study

3.4.13.1 Morphology

Scanning Electron microscopy includes preparation of thin slice from concrete specimens, selection of specimen surface for image study and taking backscattered images. The sample preparation involved cutting slice of size 2.50X2.50X0.50 cm by diamond blade saws using non aqueous lubricants, drying at low temperature and impregnating with less viscous epoxy resin, cutting grounding and polishing the epoxy impregnated concrete slice. Prepared samples were mounted on the brass stubs of Scanner using carbon tapes. Aggregates and ITZ (Interstitial Transition zone) has been selected randomly and imaged by backscattered SEM. The normal magnification used is 500X, and the pixel resolution of 512X512 (Diamond et al. 2001). However, in this study the magnification has been kept 4000X for raw materials and 200X-2000X for concrete samples. The SEM images for the raw materials (Jarosite, Cement & flyash) and concrete samples have been taken from ZEISS EVO 18 Special edition (Textile Department, IIT Delhi) and Nova Joel Special edition (MRC, MNIT, Jaipur) respectively.

3.4.13.2 Composition Analysis

The chemical composition (qualitative analysis) of jarosite and concrete samples has been determined using X-ray diffraction meter (Panalytical X) (MRC, MNIT, Jaipur). The sample preparation has been done as per the manual provided with the diffraction machine. The XRD pattern was observed by scanning the sample from 10 to 80°, 2 theta and having Cu radiation and graphite monochromatic with a current of 30 KV and a voltage of 40 MV. The concrete samples with maximum replacement (25 % jarosite) and w/c 0.45 from both the series (I & II) has been examined for knowing the predominating phases in the matrix.

CHAPTER 4

RESULTS AND DISCUSSION

In the last chapter, concrete mix design and proportioning of different raw materials in concrete mixtures has been finalized. Also, we discussed the different test procedures of experiments needed to evaluate the different properties of fresh and hardened concrete. The present chapter comprises of all the results derived from experiments performed for evaluation of different properties of concrete. Moreover, study to support in evidence of different properties of jarosite concrete has been established here.

4.1 PROPERTIES OF FRESH CONCRETE

4.1.1 Workability

The concrete mixture soon after mixing tested for its workability. Workability in terms of compaction factor of concrete mixtures (Series I & II) has been tabulated in table 4.1.

Table 4.1 Workability of fresh Concrete

Workability in terms of Compaction Factor						
Series	**I**			**II**		
	Water/cement ratio					
Jarosite (%)	**0.40**	**0.45**	**0.50**	**0.40**	**0.45**	**0.50**
0	0.98	0.97	0.96	0.96	0.97	0.96
5	0.97	0.99	0.97	0.97	0.99	0.97
10	0.96	0.98	0.96	0.97	0.98	0.96
15	0.98	0.97	0.95	0.98	0.97	0.95
20	0.96	0.96	0.97	0.98	0.97	0.97
25	0.97	0.98	0.98	0.96	0.98	0.98

The compaction factor for all the concrete mixtures (series I & II) has occurred in the range of 0.95-0.98, which can be regarded as quite a good workability. Also, the dosage of superplasticizer has been fixed for each concrete mixture to achieve desired workability (0.95-0.99).

The dosage of plasticiser in concrete mixtures (series II) seems to be lesser than mixtures in series I with same jarosite content. The reduced water demand in the concrete during mixing may be attributed to presence of fly ash. The spherical shape of fly ash decreases the water requirement in concrete (Neville 1995).

4.1.2 Density

The density of fresh concrete for series I and II has been tabulated in Table 4.2.

Table 4.2 Density of Fresh Concrete

Density (Kg/m^3)						
Series	**I**			**II**		
	Water/cement ratio					
Jarosite (%)	**0.40**	**0.45**	**0.50**	**0.40**	**0.45**	**0.50**
0	2404	2397	2389	2412	2403	2399
5	2396	2392	2376	2401	2411	2391
10	2387	2386	2366	2397	2395	2388
15	2371	2378	2359	2389	2388	2874
20	2375	2371	2368	2384	2386	2376
25	2385	2364	2371	2381	2379	2375

Density of Concrete in Series I and II seems to be reducing with rise in jarosite content. However, the reduction has been observed to be approximately 1% from control concrete to concrete with 25% sand replacement at every w/c ratio in both the series. The slight reduction in density can be attributed to addition of filler (jarosite) and mineral admixture (fly ash) having less specific gravity than cement and sand respectively.

4.1.3 Setting and Hardening of Concrete

Freshly mixed concrete, filled, compacted and casted into moulds has been kept for setting up to next 24 hours. After 24 hours, demoulding has not been possible for jarosite added concrete (excluding control mixtures) due to delay in setting and hardening of concrete. The partially set specimens have broken edges while demoulding. Jarosite concrete got demoulded after next 24 hours (48 hours after moulding) and cured. The delayed setting and hydration may be attributed to presence of lead ions in jarosite (21.875 ppm). Previous studies explained the retardation effects in concrete and mortar due formation of $Pb(OH_2)$. Portlandite reacts with lead and produces lead hydroxide which further adsorb onto C-S-H surfaces forming around hydrating cement clinker phases. (Cheeseman et al. 1999).

4.2 MECHANICAL PROPERTIES OF CONCRETE

4.2.1 Compressive strength

The compressive strength of concrete for 3, 7, 28 and 90 days for series I & II has been graphed in figure 4.1 and 4.2 respectively. Also, the values of strength has been tabulated in table no 4.1 (Series I) & 4.2(Series II).

Series I

Table 4.3 Compressive Strength of Jarosite added Concrete in N/mm^2 (Series I)

Compressive Strength* (N/mm^2)												
Age of Concrete	**3 Days**			**7 Days**			**28 Days**			**90 Days**		
Jarosite (%)	**Water /Cement Ratio**											
	0.40	**0.45**	**0.50**	**0.40**	**0.45**	**0.50**	**0.40**	**0.45**	**0.50**	**0.40**	**0.45**	**0.50**
0	20.5	19.4	16.8	31.4	25.6	23.5	38.1	31.7	30.7	38.6	33.4	32
5	19.7	19.3	16.3	27.7	25.3	20.6	34.6	30.5	27.4	36.6	33.2	29.6
10	19.4	18.9	15.7	27.4	24.6	20.13	33.6	30	26.2	35.2	31.9	28.5
15	19.2	18.3	13.1	26.3	24.7	16.9	33.7	29.9	25.5	34.5	30.6	27
20	18.8	18.6	11.2	26.7	24.2	16	32.9	29.2	24.9	34.8	30.2	26.1
25	18.5	17.6	10.6	25.7	23.8	14.7	31.4	28.8	23.9	33.8	29.5	25.3

*Average value of six specimens for each mix

The 3 days compressive strength of all the concrete was found to be decreasing with increase in jarosite content. Jarosite concrete with w/c 0.40 and 0.45 had almost similar early strength at all jarosite replacement percentages. The strength reduced from 20 N/mm^2 (control mixtures) to 17.6 N/mm^2 (25 % jarosite) in concrete samples with w/c 0.45. However, substantial reduction of 37 % with reference to control concrete was observed in maximum jarosite concrete for w/c 0.50.

At later ages (28 and 90 days), concrete with w/c 0.50 has experienced a sudden drop in strength from 10 % to 15 % fine aggregate replacement. The retardation in hardening is responsible for sudden drop of strength. Past studies revealed that the samples containing lead and zinc showed adverse effect on hydration of cement (Tashiro 1977).

Comparing strength of jarosite concrete with respect to w/c revealed different trends at different ages. In initial days, similar strengths were observed for all respective fine aggregate replacements at 0.40 and 0.45. However, at later ages, lower strength was observed with increased w/c for all respective replacement levels.

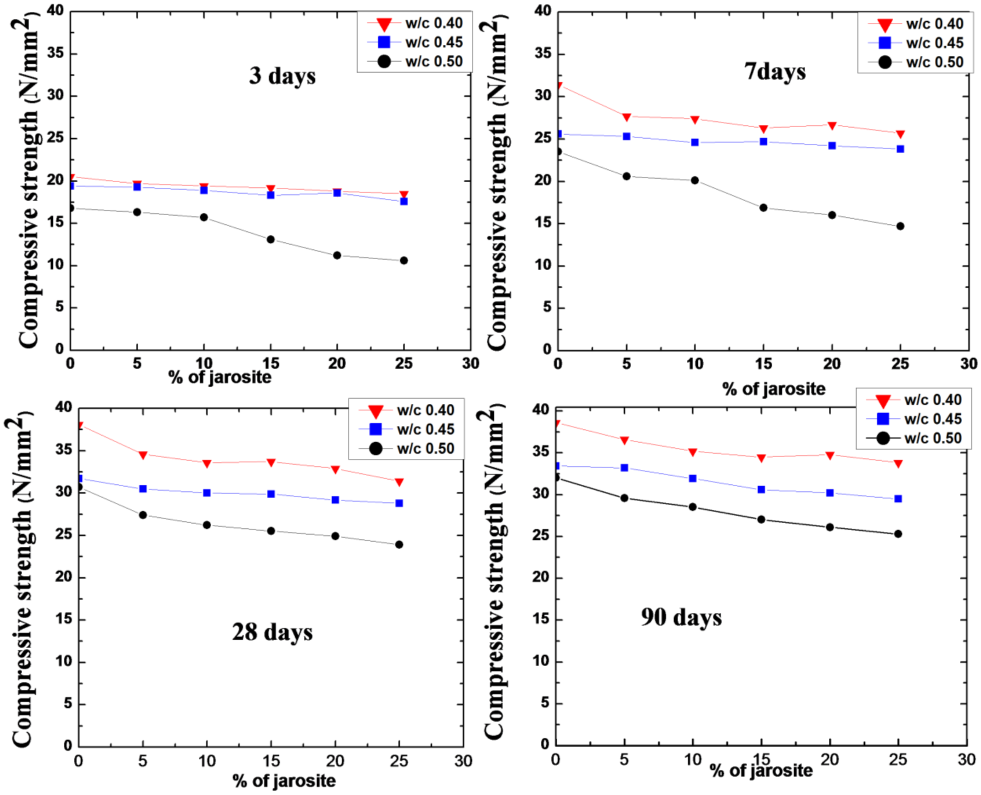


Figure 4.1 Compressive Strength of Concrete (Series I)

Series II

At the early age of 3 days, there seems an increasing trend in strength with reference to replacement levels of jarosite in concrete with all w/c ratios (0.40, 0.45 and 0.50). Moreover, concrete mixtures with w/c ratios 0.40 & 0.45 experienced almost same strength up to 20 % replacement of fine aggregates. Lower strength of the concrete samples with w/c 0.50 has been observed at all replacement levels in comparison to samples with w/c 0.40 and 0.45.

After 7 days curing, the strength following the similar trend as that of 3 days strength. However, the concrete mixtures with w/c 0.50 has achieved the strength almost similar to mixtures with w/c 0.45.

At later ages of 28 and 90 days, the strength improvement has been clearly visible in concrete mixtures with all w/c ratios (0.40, 0.45 and 0.50). In 28 days, the concrete mixtures with w/c 0.50, strength is almost constant upto 15% replacement levels and increased further till 25%.

The concrete mixtures with w/c 0.40 have obtained good strength after 28 and 90 days. Dense particle packing due to presence of fly ash and jarosite may account for good strength development with increasing jarosite content.

Table 4.4 Compressive Strength of Jarosite added Concrete in N/mm^2 (Series II)

Compressive Strength* (N/mm^2)												
Age of Concrete	**3 Days**			**7 Days**			**28 Days**			**90 Days**		
Jarosite (%)	**Water /Cement Ratio**											
	0.40	**0.45**	**0.50**	**0.40**	**0.45**	**0.50**	**0.40**	**0.45**	**0.50**	**0.40**	**0.45**	**0.50**
0	10.2	9.9	7.2	20.9	19.2	17.9	30.3	29.1	24.8	33.33	32.5	29.7
5	12.5	11.2	7.6	21	20.7	20.8	34.4	32.1	25.3	36.5	35.6	33.2
10	13.7	12.6	7.7	24.1	22.6	22.3	35.6	32.8	25.6	38.4	37.9	34.8
15	14.2	13.5	9.3	26.8	22.8	22.5	37.8	33.9	25.5	43	40.2	35.1
20	15.3	15.3	12.1	28.4	24.1	24.6	40.7	35.7	29.1	46.2	42.1	35.6
25	18.1	16.2	14.4	28.6	26.7	24.9	43.9	37.6	31.7	47.8	42.5	35.8

*Average value of six specimens for each mix

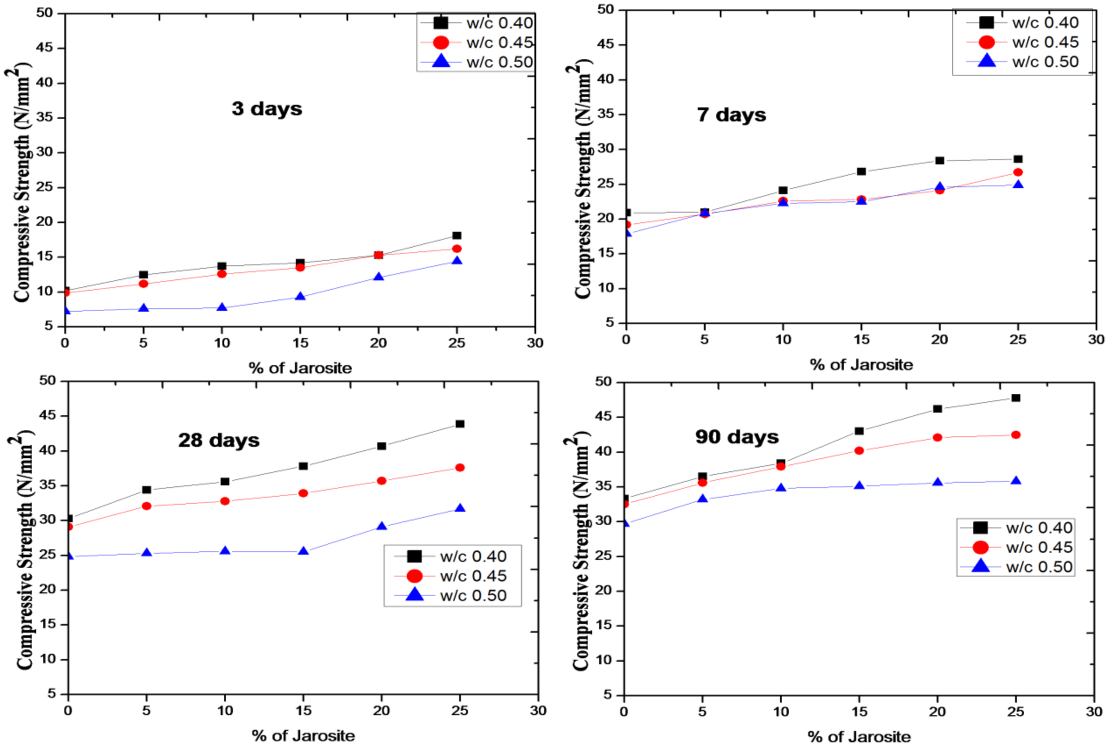


Figure 4.2 Compressive strength of Concrete (Series II)

4.2.2 Flexural strength

Flexural strength at 7 and 28 days for concrete samples is shown in figure 4.3 and tabulated in Table 4.5. In series I, the 7 days flexural strength of all the concrete mixtures containing jarosite was lower than control mixtures. Similarly, 28 days flexural strength of concrete mixtures was also less than control mixtures. Concrete mixtures up to 15 % replacement level with w/c 0.50 experienced reduction in strength and increment at 20%.

Table 4.5 Flexural Strength of Jarosite added Concrete in N/mm^2

Flexural Strength (N/mm^2)												
Series	I						II					
Age of Concrete	7 Days			28 Days			7 Days			28 Days		
Jarosite (%)	Water/Cement Ratio											
	0.40	0.45	0.50	0.40	0.45	0.50	0.40	0.45	0.50	0.40	0.45	0.50
0	4.6	4.3	4.05	5.9	5.75	5.55	3.5	3.35	2.3	5.05	4.6	4.3
5	4.35	3.95	3.75	5.8	5.6	5.0	3.6	3.55	2.35	5.4	4.75	4.6
10	4.25	3.86	3.6	5.7	5.5	4.8	3.8	3.55	2.58	5.6	4.82	5.0
15	4.15	3.75	3.4	5.75	5.3	4.9	4.1	3.72	2.96	5.75	4.8	5.2
20	4.05	3.7	3.5	5.5	5.1	4.8	4.4	4.18	3.15	5.8	5.07	5.0
25	4.05	3.5	3.3	5.1	4.85	4.65	4.55	4.4	3.4	5.85	5.15	5.11

*Average value of six specimens for each mix

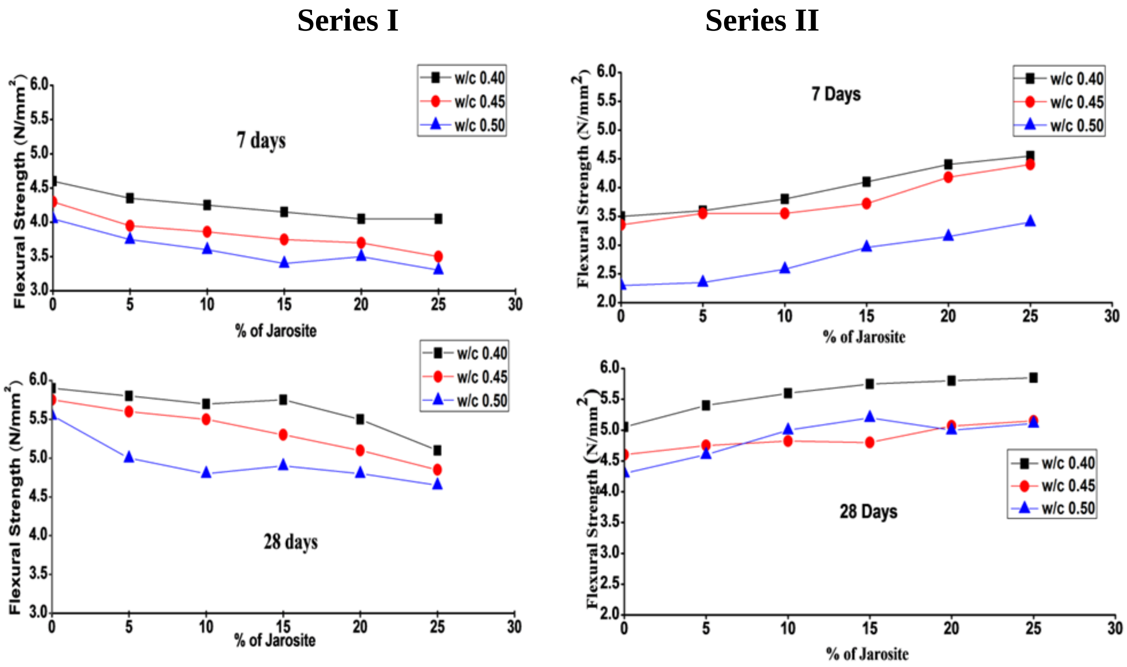


Figure 4.3 Flexural Strength of Concrete (Series I & II)

In series II, Flexural strength seems to be following almost the same trend of compressive strength. However, in 7 days, concrete mixtures with w/c 0.40 and 0.45 achieved almost same strength at all percent of jarosite while after 28 days curing, concrete mixtures with w/c 0.45 and 0.50 hold same strength at higher replacement levels.

4.3 ABRASION OF CONCRETE

The abrasion of concrete for series I & II, in terms of depth of wear is shown in table 4.6 and graphed in figure 4.4. According to IS 1237: 1980; the permissible average wear for heavy duty and general purpose floor tiles is 2 mm and 3.5 mm respectively. As the graph for concrete samples of series I depicts, all the concrete samples had the average wear within the permissible limit except for the sample with w/c 0.45 and sand replacement 25%. Moreover, the depth of wear of all the concrete samples found to be more than control samples of series I.

The concrete mixtures in series II have been experiencing reduction in abrasion as compared to control mixtures. The resistance to abrasion was more for concrete samples with fly ash.

Table 4.6 Abrasion of Concrete in terms of Wear (mm)

Abrasion In terms of wear (mm)						
Series	**I**			**II**		
	Water/cement ratio					
Jarosite (%)	**0.40**	**0.45**	**0.50**	**0.40**	**0.45**	**0.50**
0	1.42	1.48	1.56	1.51	1.484	1.49
5	1.43	1.65	1.79	1.29	1.341	1.36
10	1.47	1.7	1.88	1.21	1.24	1.29
15	1.46	1.86	1.93	1.16	1.22	1.27
20	1.56	1.92	1.96	1.10	1.147	1.19
25	1.7	2.17	2	1.01	1.07	1.13

*Average value of three specimens for each mix

On comparing compressive strength and abrasion of concrete, it was observed that as the strength decreased, abrasion in terms of depth of surface wear was increased and vice versa. Sidiqque et al. 2002, Naik et al. 2003, Li et al. 2006 also reported that the resistance of concrete to abrasion is influenced by variables such as strength, aggregate properties, surface finish and type of hardeners or toppings.

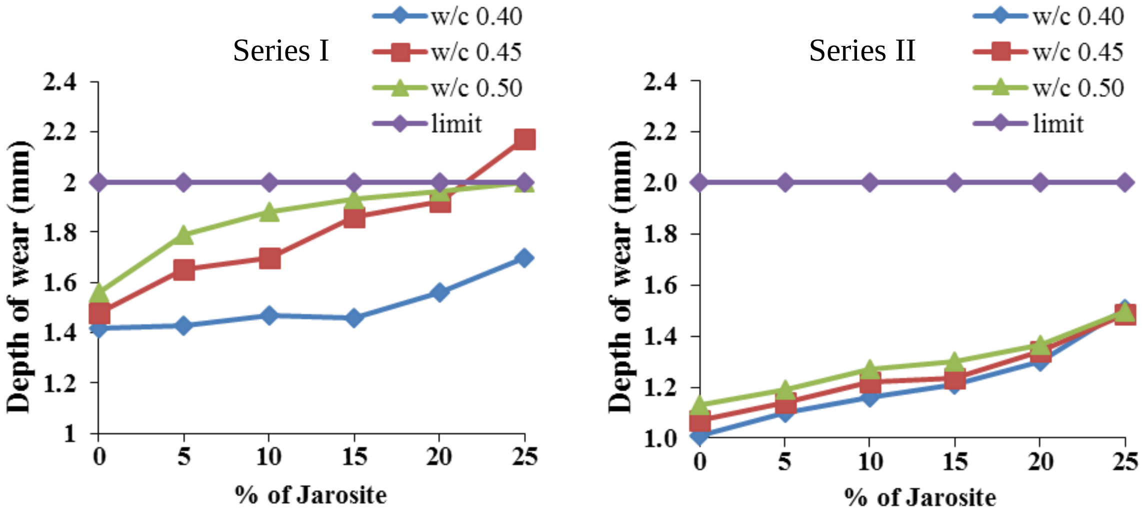


Figure 4.4 Abrasion Resistance of Concrete

4.4 WATER PERMEABILITY OF CONCRETE

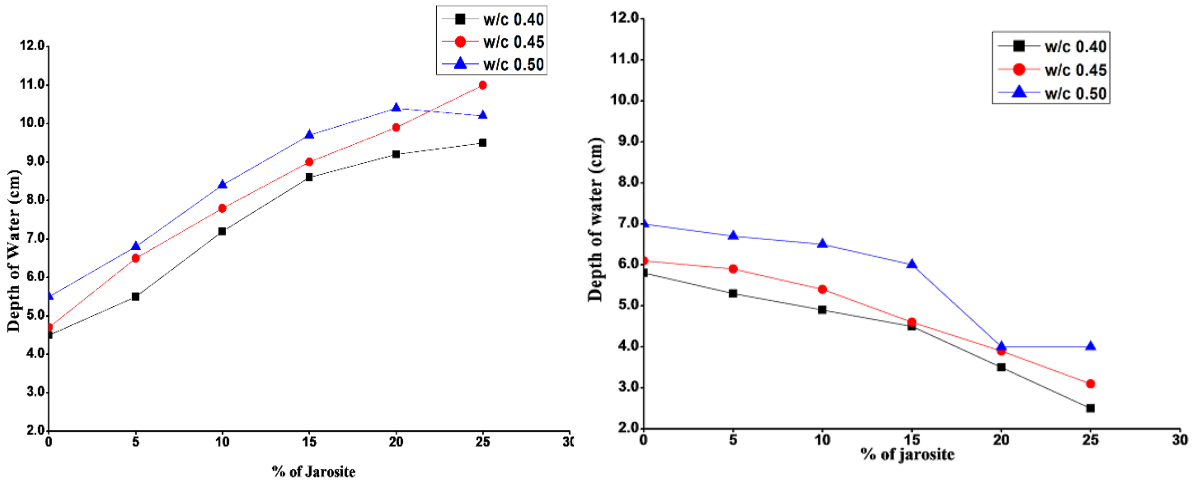
The water permeability of concrete samples (Series I & II) in terms of depth of penetration has been tabulated in table 4.7 and shown in figure 4.5. The graph of series I demonstrates the rise in depth of water penetration with increasing replacement percentage of jarosite. Addition of fly ash in II series has changed the pattern of water depth with increasing % of sand replacement. However, the magnitude of penetration depth has been lower as compared to series I concrete samples at respective fine aggregate replacement.

The control mixtures of w/c ratios 0.40 & 0.45 has high permeability range but medium permeability has been attributed by mixtures with 5% to 15% replacements and lower permeability for higher replacements. In the case of w/c 0.50, the mixtures upto 15% sand replacement fall under high permeability and further in low permeability range (as per Ganjian et al. 2009). The reduced permeability can be attributed to proper hydration and dense particle packing due to jarosite-flyash matrix, as can be seen in microscopic images of jarosite added concrete. Permeability can be controlled by restricting the movement of moisture in the concrete by modifying and refining its pore structure. This is generally achieved by the use of mineral admixtures and other pore modifying admixtures which are capable of improving the impermeability of concrete (Pawan et al. 2013). Also, Neville commented that permeability of fly ash concrete reduces with time.

Table 4.7 Water Permeability of Concrete

Water Permeability (cm)						
Series	**I**			**II**		
	Water/cement ratio					
Jarosite (%)	**0.40**	**0.45**	**0.50**	**0.40**	**0.45**	**0.50**
0	4.5	4.7	5.5	5.8	6.1	7
5	5.5	6.5	6.8	5.3	5.9	6.7
10	7.2	7.8	8.4	4.9	5.4	6.5
15	8.6	9	9.7	4.5	4.6	6
20	9.2	9.9	10.4	3.5	3.9	4
25	9.5	11	10.2	2.5	3.1	4

*Average value of three specimens for each mix



Series I **Series II**

Figure 4.5 Depth of Water Penetration of Concrete

The concrete samples showing the depth of penetration is shown in Figure 4.6 and 4.7 (darker portion is penetrated part with outlined marked in pink).

Figure 4.6 Concrete Samples (Series I) Showing Penetration of Water

Figure 4.7 Concrete Samples (Series II) Showing Penetration of Water

4.5 WATER ABSORPTION AND SORPTIVITY OF CONCRETE

4.5.1 Water Absorption

Absorption capacity of concrete samples for Series I and II in terms of percentage has been presented in table 4.8 and graphed in Figure 4.7.

Table 4.8 Water Absorption of Concrete

Water Absorption (%)						
Series	I			II		
	Water/cement ratio					
Jarosite (%)	0.40	0.45	0.50	0.40	0.45	0.50
0	1.79	2.7	3.14	2.48	2.95	3.27
5	2.41	2.92	1.7	2.12	2.57	3.17
10	2.42	3.05	2.49	2.03	2.45	2.88
15	2.5	3.06	3.24	2.01	2.42	2.59
20	2.64	3.08	4.15	1.99	2.31	2.33
25	2.85	3.11	4.66	1.97	2.07	1.63

*Average value of three specimens for each mix

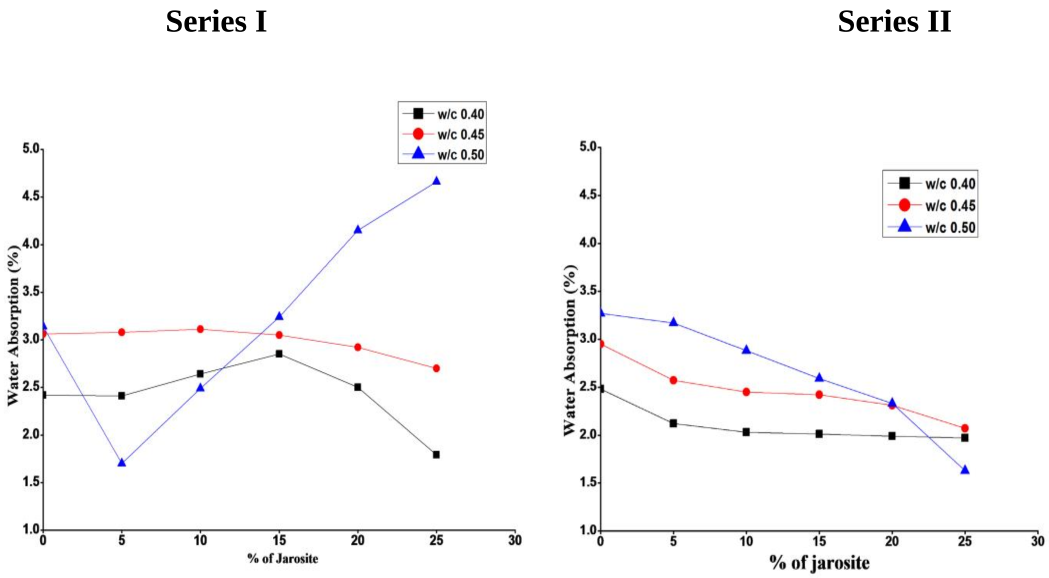

Series I **Series II**

Figure 4.8 Water Absorption of Concrete

In series I, the concrete experienced lower absorption at all water cement ratios. Perhaps, the absorption in concrete with w/c 0.50 reduced at 5% jarosite further increased linearly up to 30%. The decrement in water/cement ratio 0.45 has not been substantial. Also, the samples with w/c 0.40 showed increased absorption till 15% and then lower absorption for higher replacement levels.

However, in series II the results indicate lower absorption at higher replacement levels. The Concrete samples with w/c 0.45 & 0.50 have reached almost same absorption percent at replacement level of 20% jarosite.

4.5.2 Water Sorptivity

The values for sorptivity of water for series I & II has been tabulated in table 4.9 & 4.10 respectively. The sorption of water by concrete samples have been calculated for 10, 60 and 180 minutes and graphed in the Figure 4.9 & 4.10 for series I & II respectively.

Table 4.9 Water Sorptivity of Concrete (Series I)

Series	**I**								
Duration(mins)	**10**			**60**			**180**		
Jarosite (%)	**Water/Cement Ratio**								
	0.	**0.45**	**0.50**	**0.40**	**0.45**	**0.50**	**0.40**	**0.45**	**0.50**
0	1.	1.74	1.9	0.97	1.16	1.1	0.82	1.08	1.08
5	1.	1.74	2.53	1.1	1.23	1.55	1.08	1.12	1.23
10	1.	1.86	2.87	1.1	1.23	1.55	1.12	1.19	1.68
15	2.	1.86	3.16	1.16	1.48	2.0	1.16	1.21	1.68
20	2.	2.37	3.16	2.13	1.5	2.13	1.16	1.23	1.75
25	2.	2.69	3.16	2.13	1.55	2.13	1.23	1.23	2.01

*Average value of three specimens for each mix

Table 4.10 Water Sorptivity of Concrete (Series II)

Series	**II**								
Duration (mins)	**10**			**60**			**180**		
Jarosite (%)	**Water/Cement Ratio**								
	0.40	**0.45**	**0.50**	**0.40**	**0.45**	**0.50**	**0.40**	**0.45**	**0.50**
0	2.371	2.84	2.37	1.48	1.74	1.74	1.16	1.49	1.490
5	1.89	2.84	2.37	1.48	1.48	1.48	1.16	1.34	1.34
10	1.893	2.84	2.37	1.29	1.48	1.48	1.16	1.34	1.304
15	1.269	2.37	2.37	1.29	1.29	1.29	1.16	1.26	1.267
20	1.261	1.89	1.89	1.22	1.29	1.22	1.16	1.23	1.229
25	0.907	1.26	1.26	1.22	0.90	1.22	0.85	0.86	1.16

*Average value of three specimens for each mix

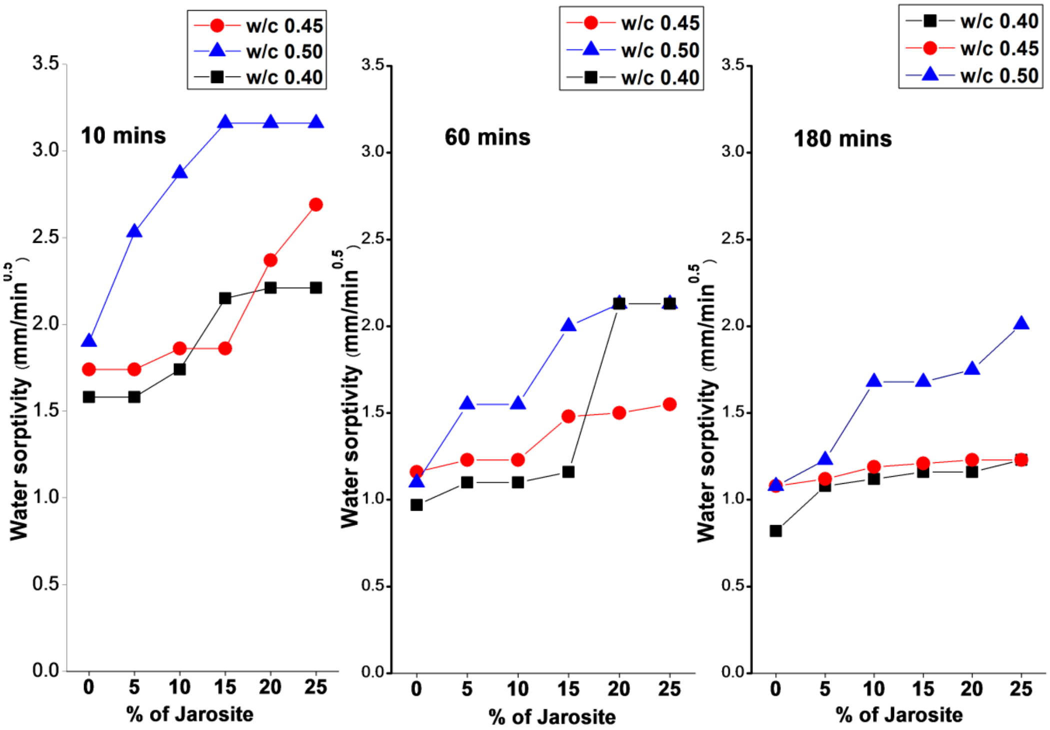


Figure 4.9 Water Sorptivity of Concrete (Series I)

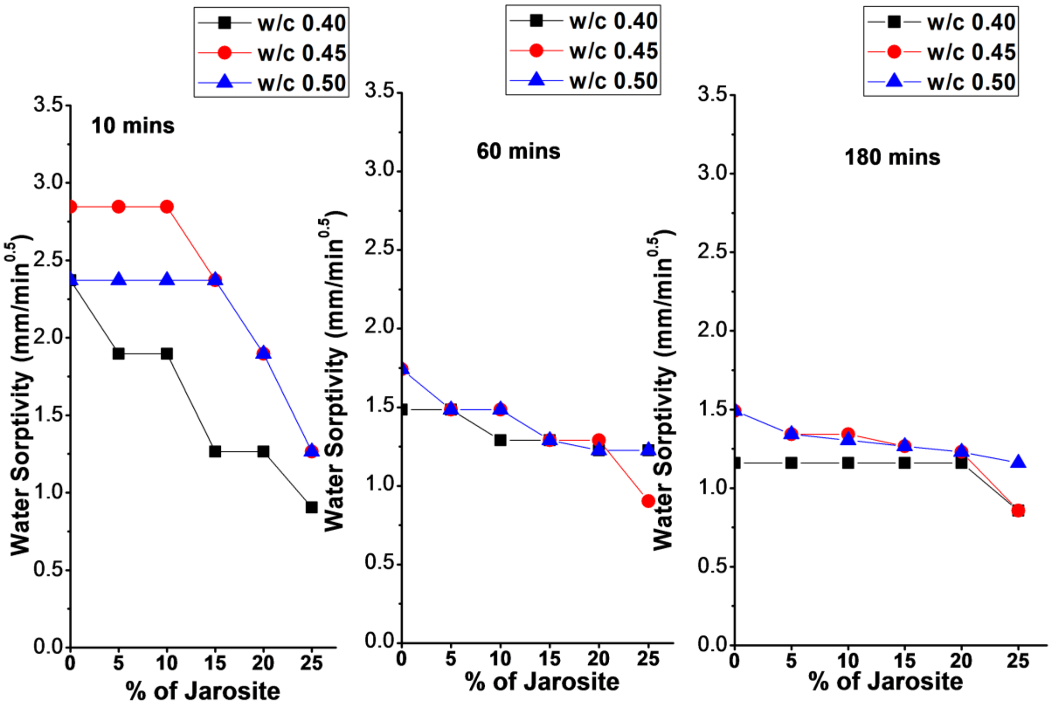


Figure 4.10 Water Sorptivity of Concrete (Series II)

Sorption in concrete had increased from control mixtures to 25% after 10, 60 and 180 minutes. At w/c ratio 0.50, water sorptivity of concrete increased linearly up to 15 % and then constant till 25%. However, the concrete with w/c ratios 0.40 & 0.50 has almost same sorption at control and 5 % and further increment. As time duration increases, the sorption capacity of concrete reduces. After 60 minutes, the trend of rise in sorptivity with increase in replacement percentage has been revealed. Slight increase in sorption has been observed concrete with w/c ratio 0.45. In concrete with w/c ratio 0.40 sorptivity increased nominally up to 15%, then rise of 95% at replacement of 20%.

In series II, After 10 minutes, the water sorptivity for concrete with w/c 0.45 has been constant upto 10% and then dropped linearly. Similar trend has been observed in samples with w/c 0.50, where constant sorption was up to 15 % and linear further. Samples with w/c 0.40 have also decreasing trend with increasing jarosite content. Sorption after 60 and 180 minutes has revealed comparable values in all three water-cement ratios. Gopalan et al. 1996 linked sorptivity with strength irrespective of age and concluded that increase in strength reduced sorption. Similarly, it has been obtained for results of our study that as strength increase, sorptivity decreased.

4.6 CARBONATION OF CONCRETE

The carbonated depth and carbonation coefficient of samples for series I (without fly ash) and II (with fly ash) has been presented in Figure 4.11 and 4.12 respectively. Also, the carbonation depth after 100 days has been presented in table 4.11 for both series.

Table 4.11 Depth of Carbonation in Concrete after 100 days

Carbonation*						
Series	**I**			**II**		
	Water/cement ratio					
Jarosite (%)	0.40	0.45	0.50	0.40	0.45	0.50
0	11	11	10	22	23	29
5	17	14	20	22	21	27
10	18	16	29	20	20	25
15	16	14	35	20	20	22
20	17	16	36	19	19	19
25	18	20	41	12	17	16

*Average value of three specimens for each mix

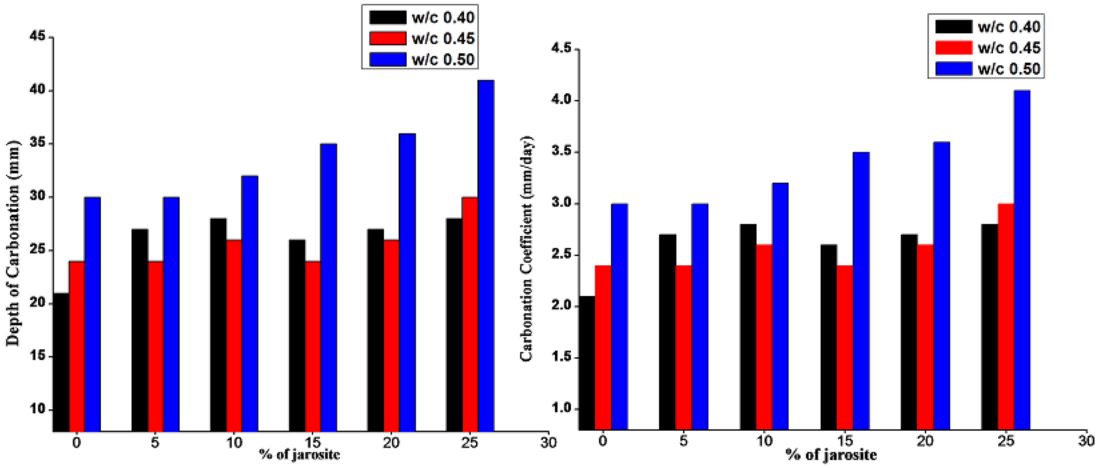


Figure 4.11 Carbonation Depth and Co-Efficient of Concrete (Series I)

The carbonated depth in concrete samples has not followed any specific pattern except that of samples with w/c 0.50. More carbonation with more jarosite content has been observed in samples with w/c ratio 0.50. Concrete with w/c 0.40 has shown comparable depth of carbonation at different percentage of jarosite except at control sample.

Maximum carbonated depth of 42 mm has been revealed in concrete with w/c 0.50 and 25% jarosite.

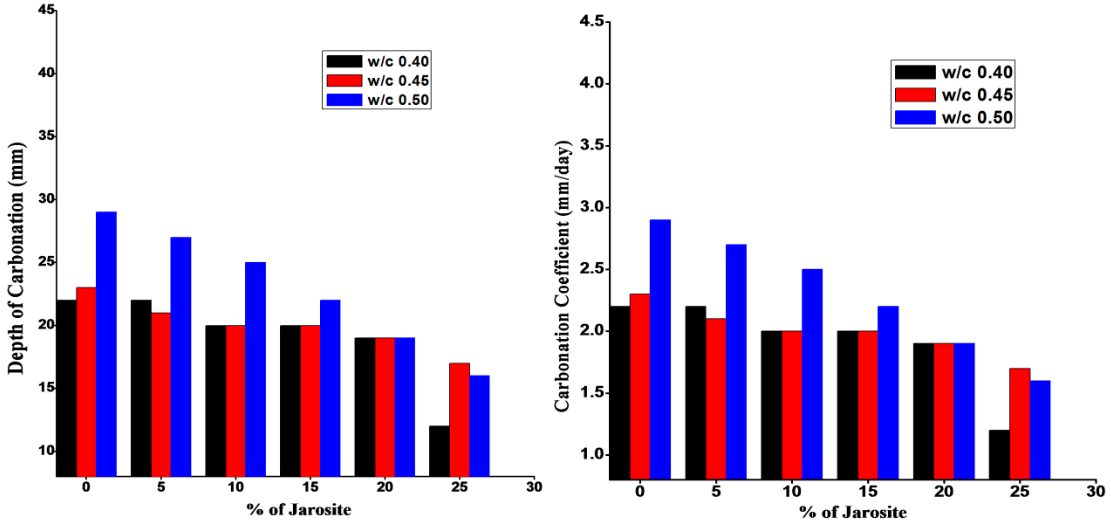


Figure 4.12 Carbonation Depth and Co-efficient of Concrete (Series II)

The graph in figure 4.12 illustrates that the depth of carbonation has reduced with increase in jarosite content of concrete samples. In mixtures with w/c 040, the drop in carbonation seems to be linear upto 20 % jarosite and became constant further. but, the concrete mixtures with w/c 0.45 had experienced comparable decrement with jarosite content. In case of concrete samples with w/c 0.50, the reduction has been observed to be linear throughout the replacement levels.Also, the concrete samples with w/c 0.40 has substantially lower carbonation depth as compared to samples with other w/c ratios (0.45 & 0.50) at all the respective replacement levels (excluding control samples).

The main factors affecting concrete carbonation are the type and the content of binder, water/binder ratio, the degree of hydration, the exposure condition (concentration of CO2, and relative humidity). (Jianga et al. 2000).

Figure 4.13 & 4.14 illustrates the concrete samples examined for carbonation depth after 100 days, using phenopthalein indicator for series I & II respectively. The indicator giving purplish red colour on concrete and changes to colourless on carbonated portion.

Figure 4.13 Samples Showing Carbonated Depth of Sliced Samples for Series I

;

Figure 4.14 Samples Showing Carbonated Depth of Sliced Samples for Series II

4.7 CHLORIDE ION DIFFUSIVITY OF CONCRETE

Table 4.12 represents the steady state diffusion of chloride ions in the concrete (Series I in left and series II in right) in terms of diffusivity coefficient. The values of diffusion co-efficient in terms of Dssm have been graphed in figure 4.15. In series I, chloride diffusion increased when jarosite content increased. For w/c 0.40, the chloride diffusion increased linearly upto 15% then constant for 20% and increased further. Concrete with w/c 0.50 linearly increased chloride diffusion with increased percent of jarosite. The maximum diffusivity of 8.5 X 10^{-12} m^2/s occurred for concrete with w/c 0.50 and 25% jarosite.

In series II, the chloride diffusion reduced with rise in jarosite content. The concrete with w/c 0.40 has substantial decrement from 8 X 10^{-12} m^2/s for control mixture to 5.74 X 10^{-12} m^2/s for maximum content of jarosite (25 %). In control mixtures with w/c 0.45 & 0.50, the diffusity of concrete was almost same. The excess C-S-H formation acts as a thick impermeable membrane for the ingress of chloride ions into concrete. This would make the concrete more resistant to aggressive environment (Chopra et al. 2015).

Table 4.12 Chloride Ion Diffusivity in Concrete

Chloride Ion Diffusion*						
Series	I			II		
	Water/cement ratio					
Jarosite (%)	0.40	0.45	0.50	0.40	0.45	0.50
0	4.5	4.7	5.5	5.8	6.1	7
5	5.5	6.5	6.8	5.3	5.9	6.7
10	7.2	7.8	8.4	4.9	5.4	6.5
15	8.6	9	9.7	4.5	4.6	6
20	9.2	9.9	10.4	3.5	3.9	4
25	9.5	11	10.2	2.5	3.1	4

*Average value of three specimens for each mix

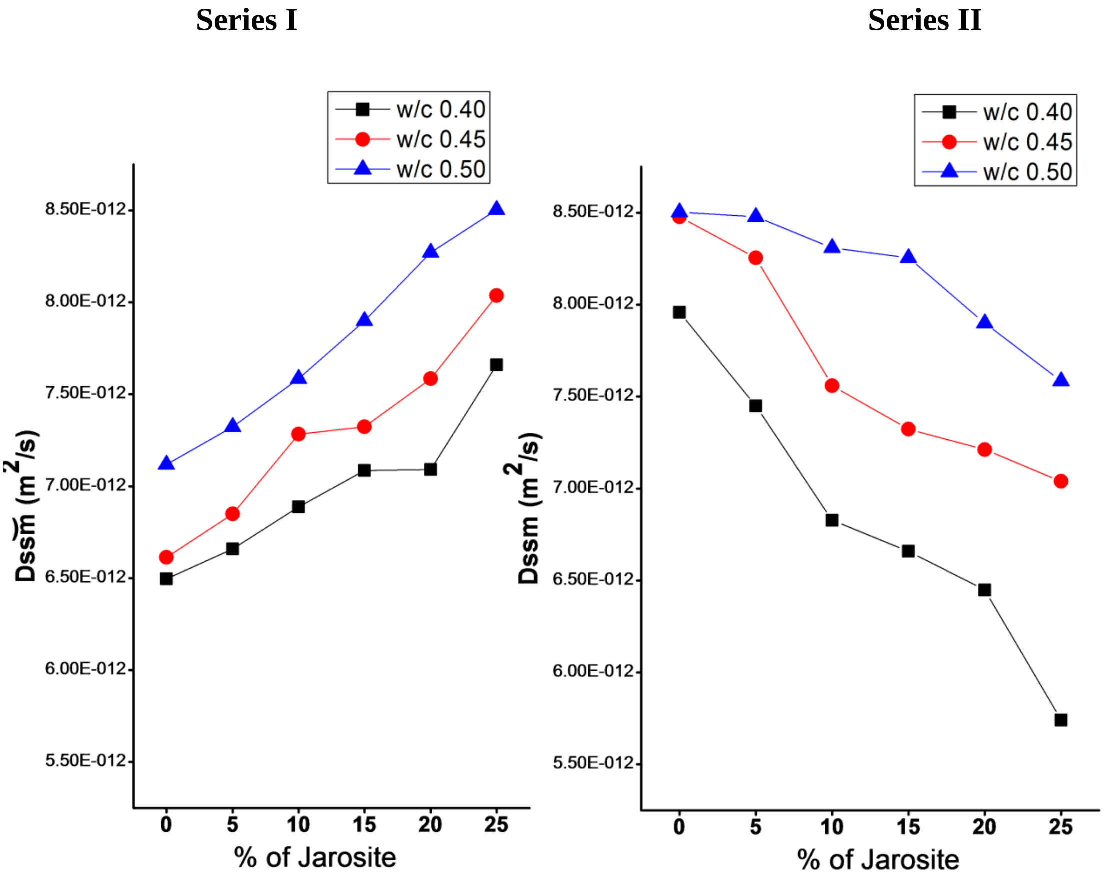

Series I **Series II**

Figure 4.15 Chloride Ion Diffusivity of Concrete

4.8 CHLORIDE ION PENETRATION

Figure 4.16 and 4.17 show the results of Chloride ion penetration in Concrete specimen at 28 and 56 days respectively. Also, the results being tabulated in Table 4.13 and 4.14 respectively. After 28 days of immersion, the graph indicates that the chloride penetration increases with increase in jarosite content. However, in series II the chloride penetration reduced with increased jarosite.

In series I, after 28 days of immersion in NaCl solution, the penetration of chloride ion in 25 % jarosite added concrete was 30-40 % higher than control specimen, for all the three w/c ratios (0.40, 0.45 and 0.50). However, after 56 days the increase in ion penetration has been calculated in the range of 20-25% at higher jarosite content. At w/c 0.50, few concrete specimen showed same penetration levels (12 mm penetration at 10 and 15 % jarosite content and 13 mm penetration at 20 and 25%). Considering w/c ratio, it can be predicted that ingress of chloride ion increased at higher w/c ratio.

However the graphs of series II depicts opposite behavior of chloride ion penetration with respect to amount of jarosite in concrete. Concrete exhibited resistance to chloride ion penetration with higher jarosite content. In 28 days the maximum increase in resistance has been measured as 25% in jarosite concrete (w/c 0.40 and 25 % jarosite) when compared with control specimen. Samples with w/c 0.45 and 0.50 experienced reduced penetration of ions in the range of 20-25% for jarosite concrete with respect to control mixtures.

Table 4.13 Chloride Ion Penetration of Jarosite in 28 days

Chloride Ion Penetration* (mm)						
Series	**I**			**II**		
	Water/cement ratio					
Jarosite (%)	**0.40**	**0.45**	**0.50**	**0.40**	**0.45**	**0.50**
0	8	9	10	8	9	9
5	9	10	11	8	9	8
10	10	11	12	7	8	8
15	11	12	12	8	8	7
20	12	13	13	7	8	8
25	13	14	13	6	7	7

*Average value of three specimens for each mix

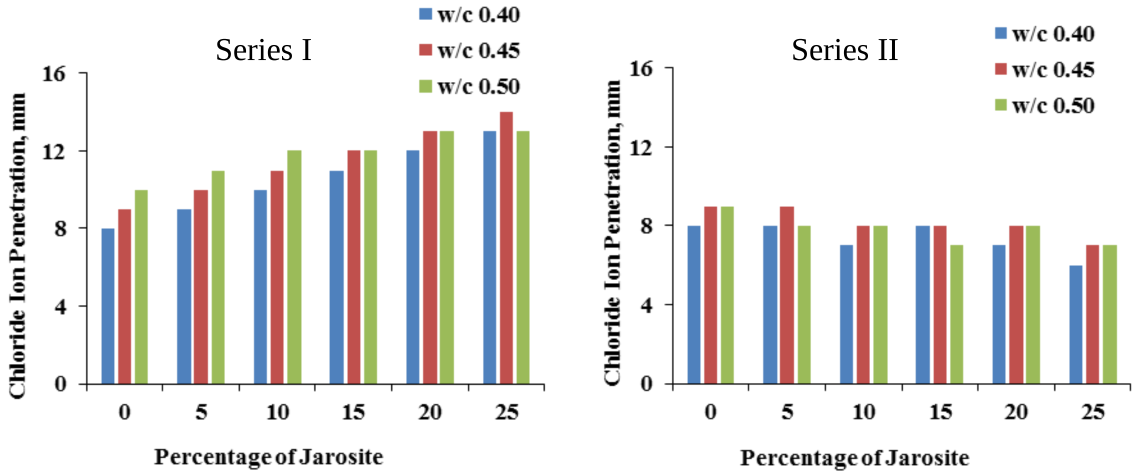


Figure 4.16 Chloride Ion Penetration of Jarosite in 28 days

At later age (56 days), the percentage of reduced ions been calculated in the range of 12-15% for jarosite concrete for all water/cement ratios. Also, the graph depicts same magnitude of chloride ingress in different jarosite concrete specimens. In w/c ratio 0.40, samples with 0, 5 and 15% jarosite have 8 mm penetration and samples with 10 and 20 % jarosite have 7 mm penetration. In w/c 0.45, samples with 0 and 5 percent jarosite have 9mm, specimen with 10, 15 and 20 % jarosite have value of penetration as 8mm. for specimens with w/c 0.50, similar penetrations are observed at 5, 10 and 20 % replacement levels (8 mm) and at 15 and 25 % replacement levels (9 mm).

Table 4.14 Chloride Ion Penetration of Jarosite in 56 days

Chloride Ion Penetration* (mm)						
Series	**I**			**II**		
	Water/cement ratio					
Jarosite (%)	**0.40**	**0.45**	**0.50**	**0.40**	**0.45**	**0.50**
0	12	14	15	13	14	14
5	13	14	16	13	13	14
10	13	11	17	12	12	14
15	14	12	18	12	13	13
20	14	13	18	11	11	13
25	15	17	18	11	12	13

*Average value of three specimens for each mix

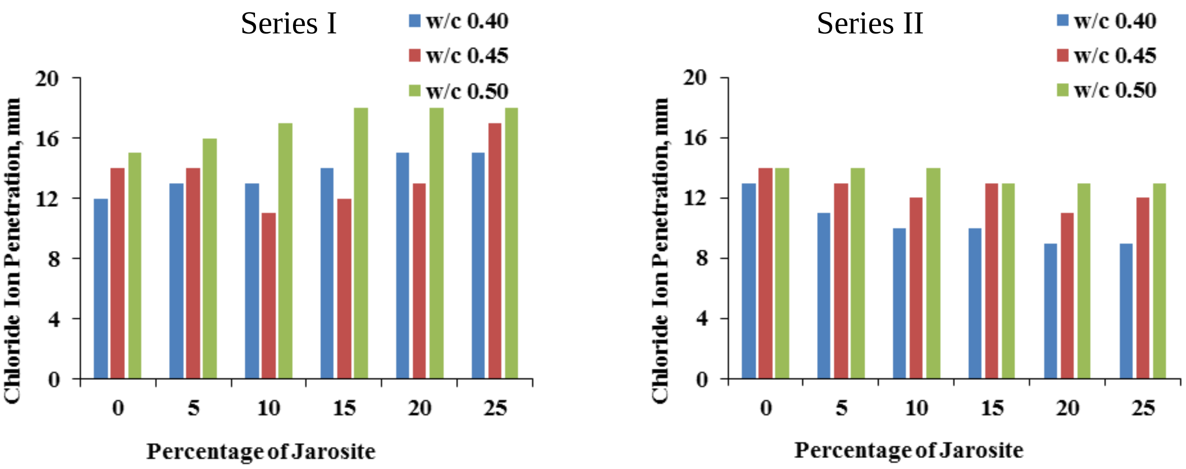


Figure 4.17 Chloride Ion Penetration of Jarosite in 56 days

The Experimental test results support the study by Guneyisi et al. 2007, 2009 which indicated that cement type, w/c ratio, curing condition, and testing age were very effective on the chloride permeability of concretes.

The Cl (%) for admixed concrete was lower than the control mix irrespective of the age of concrete suggesting refinement of microstructure leading to improvement in durability properties of concrete (Ransinchung et al. 2009). Similarly, use of fly ash in II series lowered the penetration of chloride ions as compared to control specimens at 28 and 56 days.

4.9 CORROSION IN REINFORCEMENT OF CONCRETE

The resistance to corrosion in reinforced concrete for series I & II after 15, 30, 45, 60, 75 and 90 days have been tabulated in table 4.15 and graphed in figure 4.18. The corrosion measured as potential has been shown for J1, J6, J7, J12, J13 and J18 in series I and F1, F6, F7, F12, F13 and F18 in series II. In series I, the corrosion resistance has been less negative for control mixtures compared to mixtures with maximum replacement of 25%. As per the ASTM C 876, if potentials over an area are more positive than 0.20 V CSE, there is a greater than 90% probability that no reinforcing steel corrosion is occurring in that area at the time of measurement. If it is in between 0.20 and 0.35 V CSE corrosion activities in that area uncertain and if it is more negative than 0.35 V CSE there is greater than 90% probability that reinforcing steel corrosion is occurring in that area**.**

Table 4.15 Resistance of Corrosion in Concrete

Corrosion* (cm)						
Series	**I**			**II**		
	Water/cement ratio					
Jarosite (%)	**0.40**	**0.45**	**0.50**	**0.40**	**0.45**	**0.50**
0	4.5	4.7	5.5	5.8	6.1	7
5	5.5	6.5	6.8	5.3	5.9	6.7
10	7.2	7.8	8.4	4.9	5.4	6.5
15	8.6	9	9.7	4.5	4.6	6
20	9.2	9.9	10.4	3.5	3.9	4
25	9.5	11	10.2	2.5	3.1	4

*Average value of three specimens for each mix

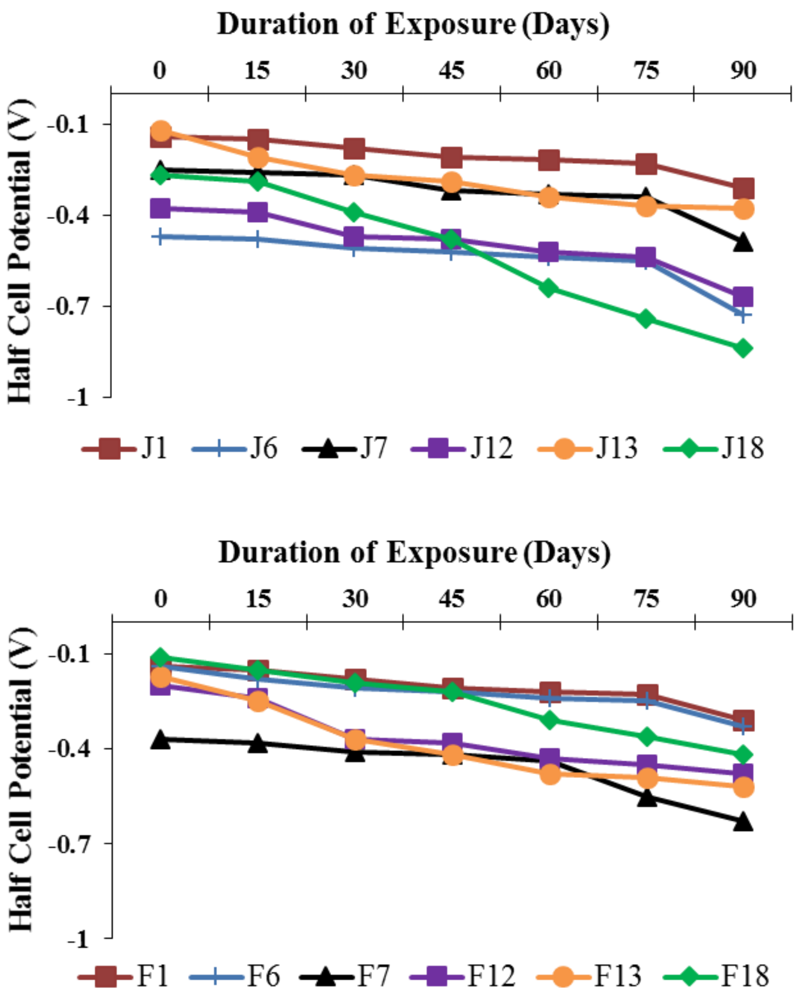


Figure 4.18 Resistance of Corrosion of Reinforcement in Concrete

Figure 4.19 Connections of Bars for Half Cell Potential

In the graph shown, the control concrete mixtures F1 (w/c 0.40) & F13 (w/c 0.50) has less negative potential than other concrete mixtures in figure 4.18. After 90 days, the concrete mixtures with maximum replacement levels at all three w/c ratios have more negative potential than 0.35 V, indicating probability that reinforcement will be corroded.

4.10 TOXICITY LEACHING POTENTIAL TEST OF HEAVY METALS IN CONCRETE

Test was conducted on raw jarosite and jarosite concrete with maximum fine aggregate replacement at different w/c. The results were tabulated in Table 4.16. The leaching of zinc and copper in raw jarosite (231.818 ppm and 0.55 ppm) is lower than limits (500ppm and 5ppm) given in United State Environmental Protection Agency (USEPA). However, the leaching of lead, cadmium and iron (21.875 ppm, 5.35ppm and 130 ppm) seems higher than permissible limits (5 ppm, 1 ppm and 30 ppm) of USEPA. Also, the leaching of all metals in the tested concrete mixtures was within the permissible limits as per USEPA. The leaching of zinc and copper in raw jarosite (231.818 ppm and 0.55 ppm) is lower than limits (500ppm and 5ppm) given in United State Environmental Protection Agency (USEPA). However, the leaching of lead, cadmium and iron (21.875 ppm, 5.35ppm and 130 ppm) seems higher than limits (5 ppm, 1 ppm and 30 ppm) of USEPA. The concrete mixtures with highest jarosite percent (25%) at all w/c ratios seem to have lower leaching values of heavy metals as per the limiting values in USEPA.

Table 4.16 Toxicity Leaching Of Raw Materials and Concrete

Sample			**Heavy elements (ppm)**				
w/c	**Jarosite (%)**	**Fly Ash (%)**	**Zinc**	**Lead**	**Copper**	**Cadmium**	**Iron**
0.40	**25**	**0**	1.864	2.25	0.0643	0.0085	11
0.45	**25**	**0**	3.961	2.24	0.108	0.581	14
0.50	**25**	**0**	1.455	2.875	0.057	0.0095	16
0.40	**25**	**25**	3.409	3.25	0.107	0.009	27.5
0.45	**25**	**25**	2.864	1.25	0.085	0.007	15
0.50	**25**	**25**	3.681	2.313	0.0071	0.215	10.5
Raw Jarosite			231.818	21.875	0.55	5.35	130
Limits as per USEPA			**500**	**5**	**5**	**1**	**30**

4.11 SULPHATE ATTACK

4.11.1 Increase in Weight of sulphate attacked specimen

Figure 4.20 and table 4.17 represents the increase in weight of sulphate attacked specimen after 28 days immersion in $MgSO_4$ solution.

Table 4.17 Increase in weight of Sulphate Attacked Concrete Specimen

Increase in weight (%)						
Series	**I**			**II**		
	Water/cement ratio					
Jarosite (%)	**0.40**	**0.45**	**0.50**	**0.40**	**0.45**	**0.50**
0	0.15	0.16	0.18	0.15	0.17	0.18
5	0.14	0.17	0.18	0.14	0.16	0.19
10	0.16	0.17	0.19	0.16	0.16	0.18
15	0.14	0.18	0.21	0.14	0.15	0.18
20	0.17	0.2	0.2	0.14	0.14	0.17
25	0.18	0.2	0.22	0.13	0.14	0.16

*Average value of three specimens for each mix

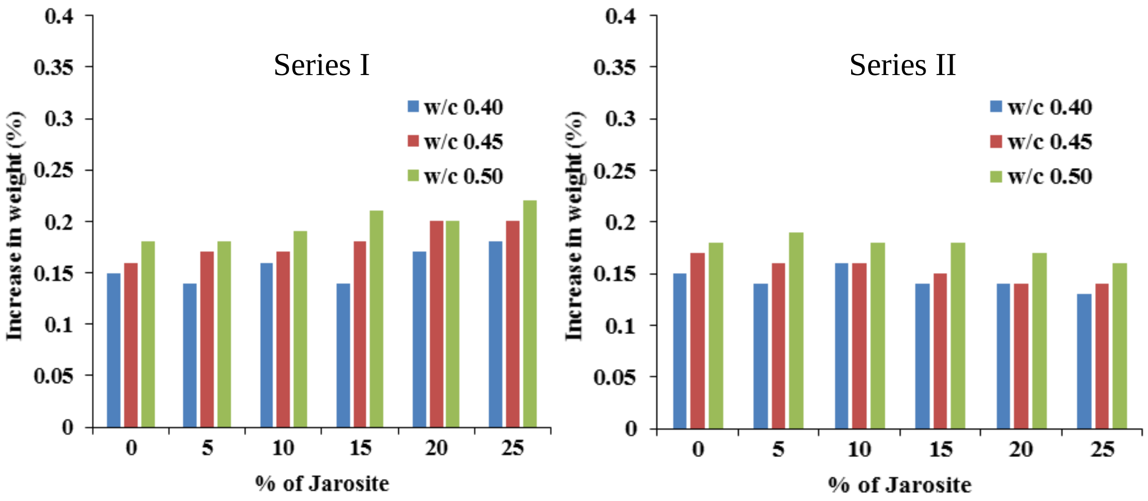


Figure 4.20 Increase in weight of sulphate attacked specimen in 28 days

It can be noticed from graph that after 28 days of immersion in magnesium sulphate solution, percentage of weight increase in concrete samples followed increased trend in series I and decreasing trend in series II. The increase in Series I and decrease in Series II is statically negligible.

Similar pattern has been observed at the end of 56 days immersion. From 28 to 56 days, there has been gradual increase in weight of the specimen in series I and II. However, the percentage of increase in weight of concrete specimens in series II has been recorded lower as compared to specimens in series I. The lesser weight indicates lesser penetration of sulphate solution in concrete.

Table 4.18 Increase in weight of sulphate attacked specimen in 56 days

Increase in weight (%)						
Series	**I**			**II**		
	Water/cement ratio					
Jarosite (%)	**0.40**	**0.45**	**0.50**	**0.40**	**0.45**	**0.50**
0	0.31	0.31	0.32	0.3	0.32	0.33
5	0.3	0.31	0.33	0.29	0.32	0.31
10	0.32	0.32	0.33	0.29	0.3	0.3
15	0.32	0.33	0.34	0.28	0.29	0.3
20	0.33	0.34	0.35	0.27	0.29	0.29
25	0.35	0.34	0.35	0.28	0.27	0.29

*Average value of three specimens for each mix

Figure 4.21 Increase in weight of sulphate attacked specimen in 56 days

Pozzolanic reactions consume CH and generate additional C–S–H, which promotes densification and lowers permeability of paste (Al-Amoudi et al. 1995, Mehta et al. 2008, Veiga et al. 2012). The results in series II have dense matrix due to fly ash as binder, which lowered the permeability and weight loss in jarosite concrete.

4.11.2 Loss in Compressive Strength of Attacked Specimen

Figure 4.22 and table 4.19 show the loss of compressive strength in sulphate attacked concrete specimens.

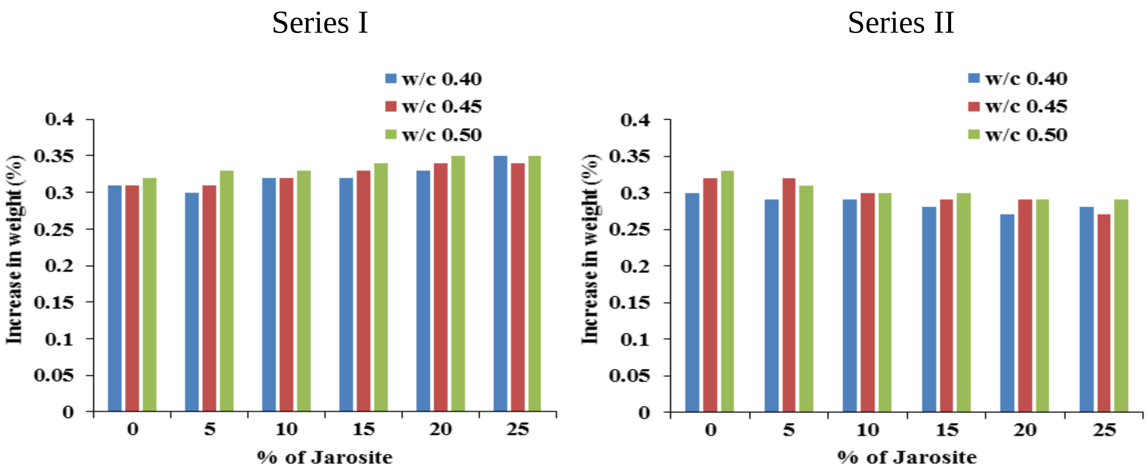


Figure 4.21 Increase in weight of sulphate attacked specimen in 56 days

Table 4.19 Loss in Compressive Strength after 56 days of Immersion.

Loss in Compressive Strength* (%)						
Series	**I**			**II**		
	Water/cement ratio					
Jarosite (%)	**0.40**	**0.45**	**0.50**	**0.40**	**0.45**	**0.50**
0	0.57	0.60	0.70	0.59	0.62	0.65
5	0.61	0.68	0.74	0.52	0.58	0.60
10	0.67	0.75	0.79	0.54	0.51	0.57
15	0.73	0.79	0.83	0.48	0.53	0.55
20	0.78	0.81	0.92	0.43	0.50	0.52
25	0.85	0.86	1.07	0.41	0.46	0.49

*Average value of three specimens for each mix

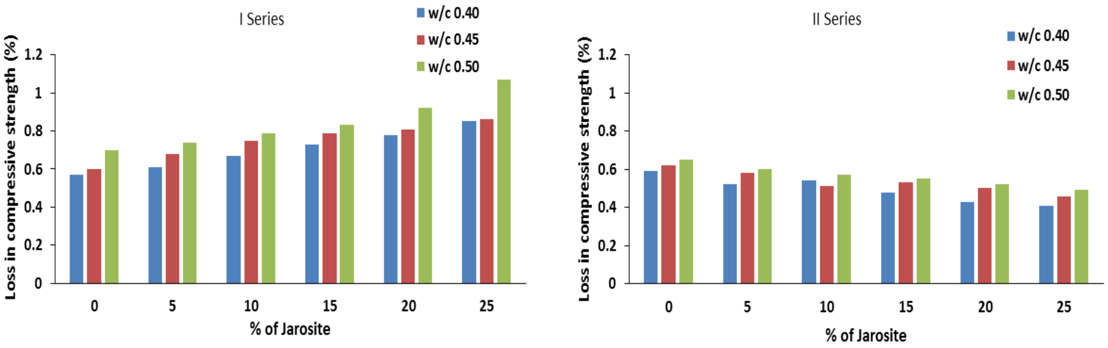


Figure 4.22 Loss in Compressive Strength of Sulphate Attacked Specimen in 56 Days

The graph of loss in compressive strength in suphate attacked concrete showed similar behavior of mass loss. Series I experienced increase in strength loss of sulphate specimens with increase in jarosite content. However, the attacked specimens in series II has lesser loss in strength at higher jarosite content. Fly Ash –jarosite dense matrix and pozzolanic reactions has been responsible for lesser loss in strength. Pozzolanic binders reduced loss in compressive strength of the mg-sulphate attacked specimen (Behfarnia et al. 2013).

4.12 MICROSCOPIC INVESTIGATIONS

4.12.1 SEM Analysis

The microscopic images of jarosite added concrete (series I & II) has been scanned and presented. The images of concrete with jarosite (without fly-ash) have been shown from figure 4.23 – figure 4.29 for different w/c ratios (0.40, 0.45 and 0.50) and different jarosite content. Similarly, images of concrete with jarosite and fly-ash have been shown in figure 4.30 – figure 4.36.

Microscopic study of concrete specimen illustrates that images for series I (figure 4.23 – 4.29) depicts more prominent cracks at ITZ (interstitial transition zone) as compared to images for series II (figure 4.30-4.36).

In series I, on comparing control concrete specimen (Figure 4.23) with jarosite concrete, lesser and finer cracks has been visualized for control specimen. Also, jarosite concrete specimen (25 % jarosite and w/c 0.40) shown in figure 4.24 has wider cracks at ITZ in comparison to other specimens of jarosite concrete.

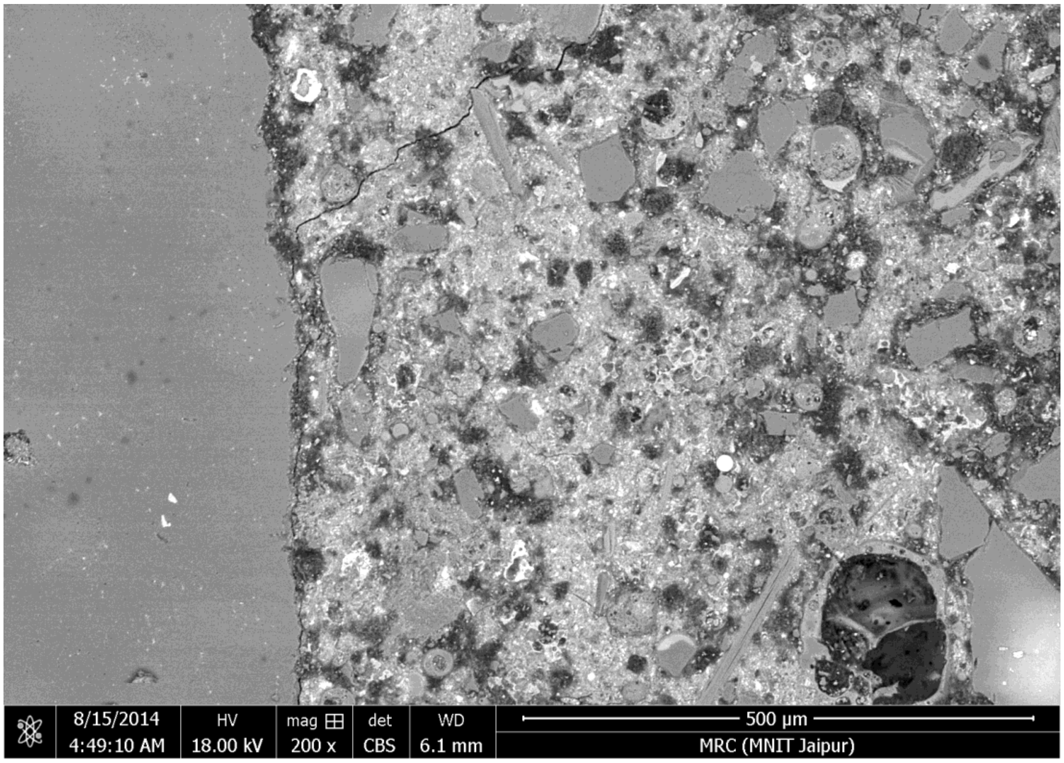


Figure 4.23 SEM Image of Control Concrete with W/C 0.40 (Series I)

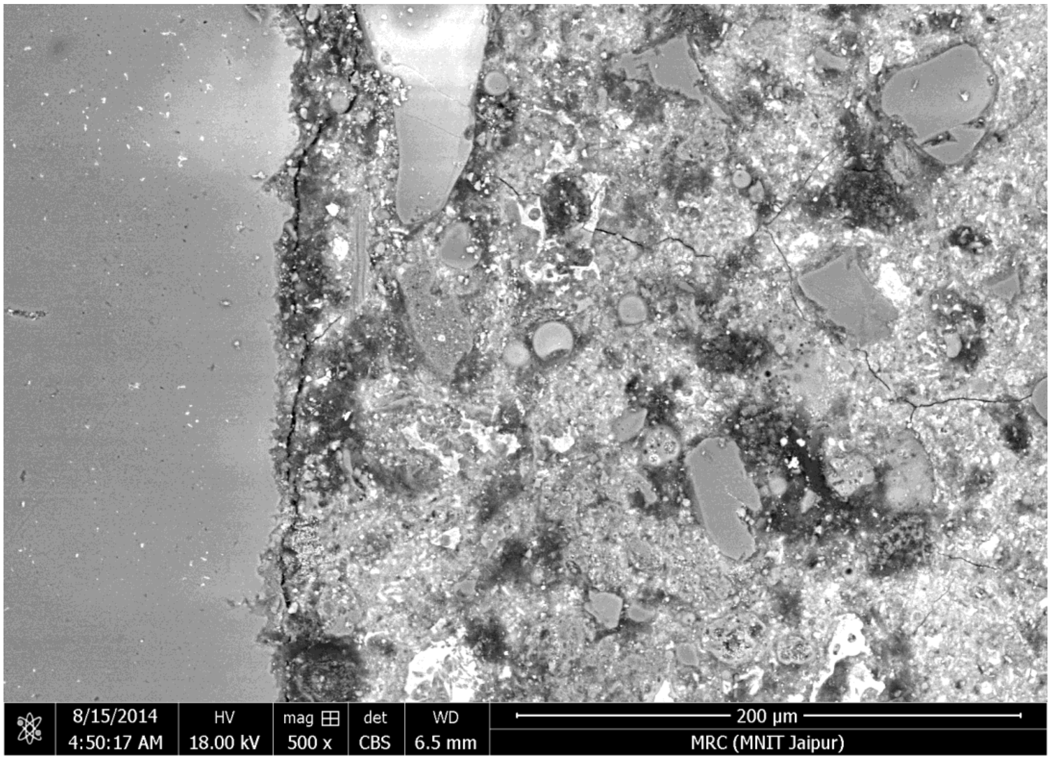


Figure 4.24 SEM Image of Concrete with W/C 0.40 & 5 % Jarosite (Series I)

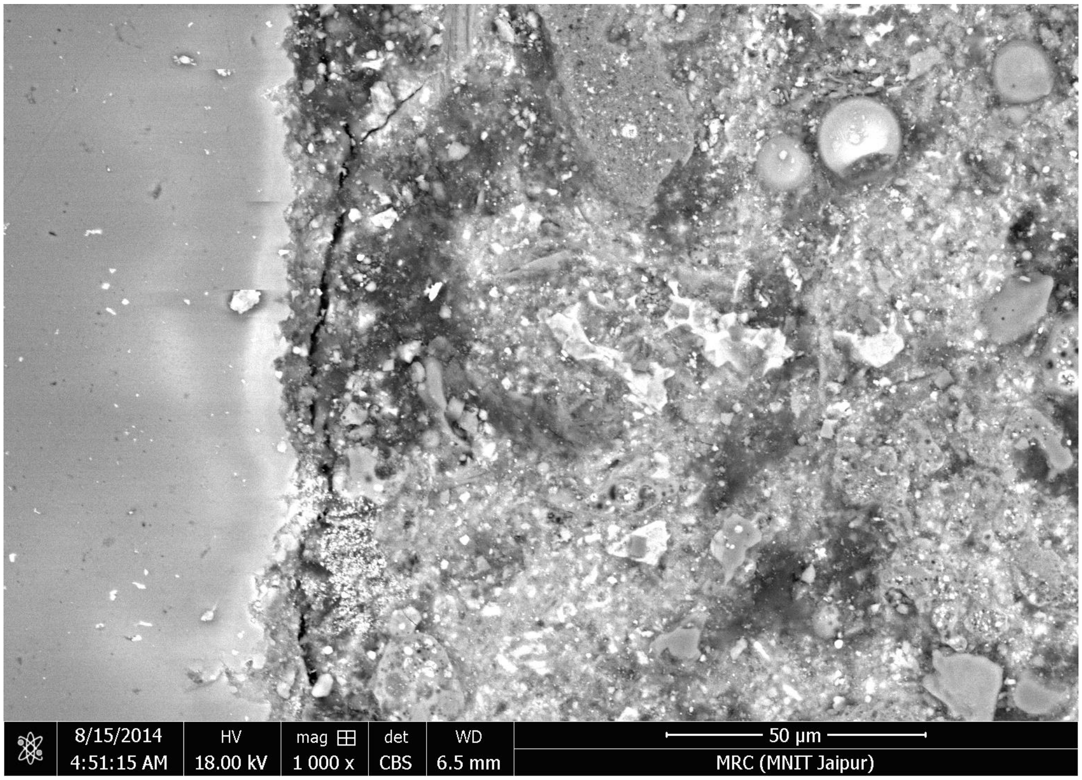


Figure 4.25 SEM Image of Concrete with W/C 0.40 & 25 % Jarosite (Series I)

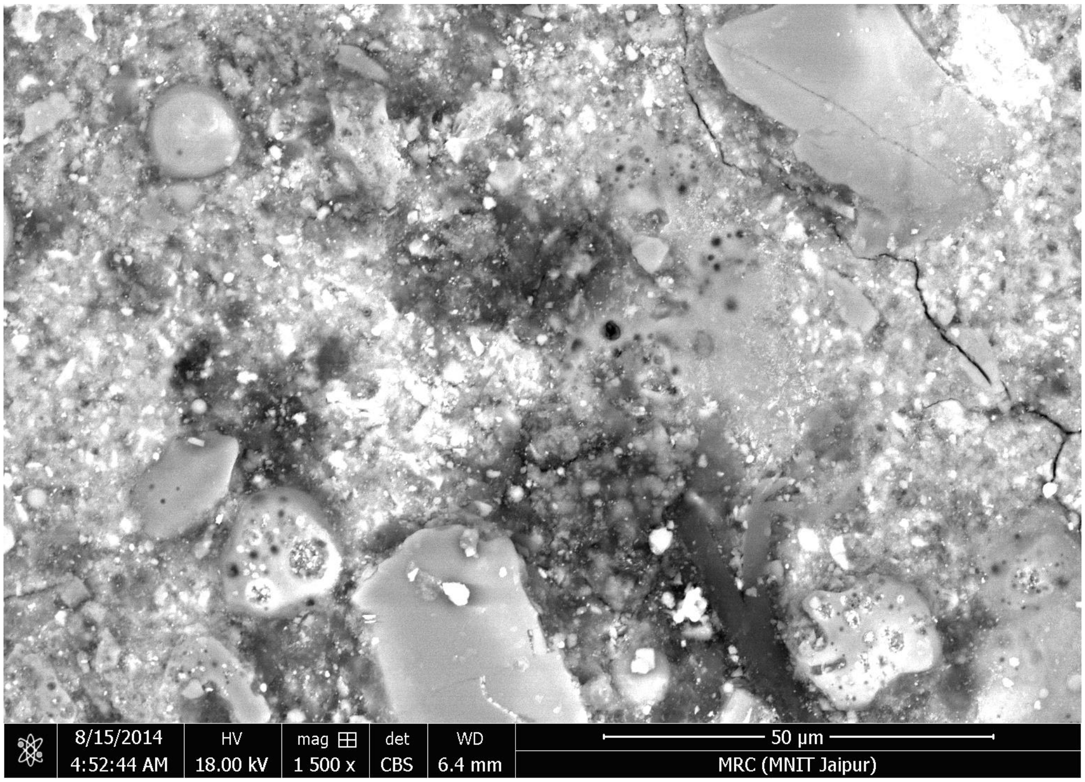


Figure 4.26 SEM Image of Concrete with W/C 0.45 & 5 % Jarosite (Series I)

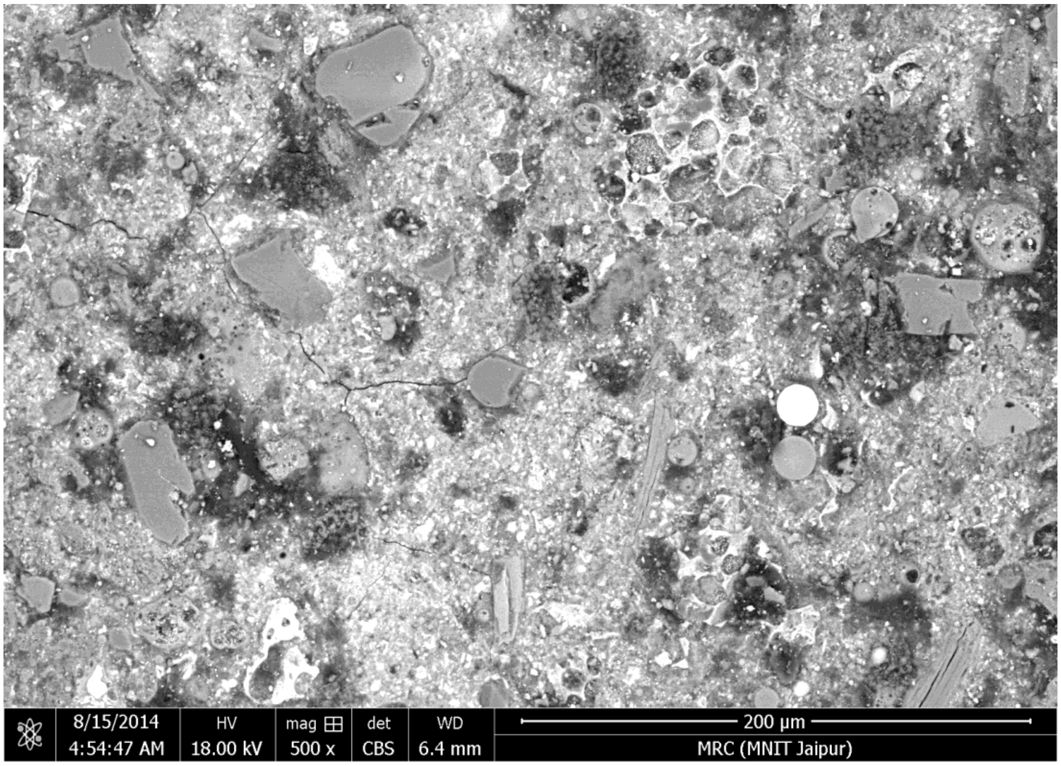


Figure 4.27 SEM Image of Concrete with W/C 0.45 & 25 % Jarosite (Series I)

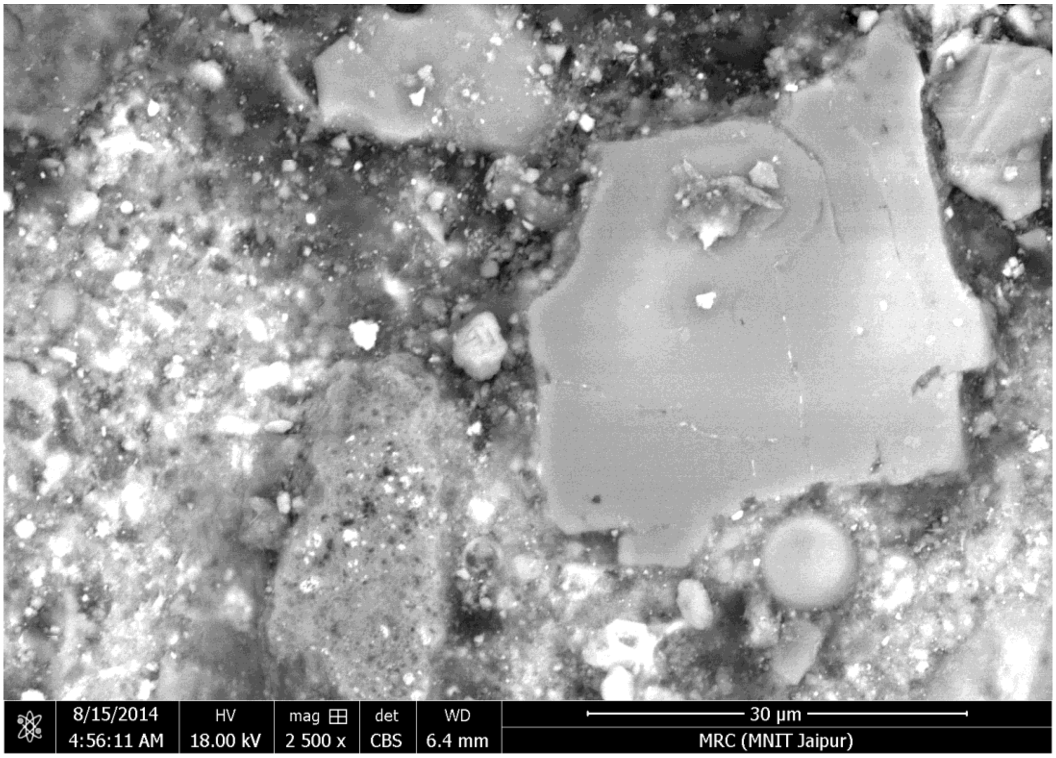


Figure 4.28 SEM Image of Concrete with W/C 0.50 & 5 % Jarosite (Series I)

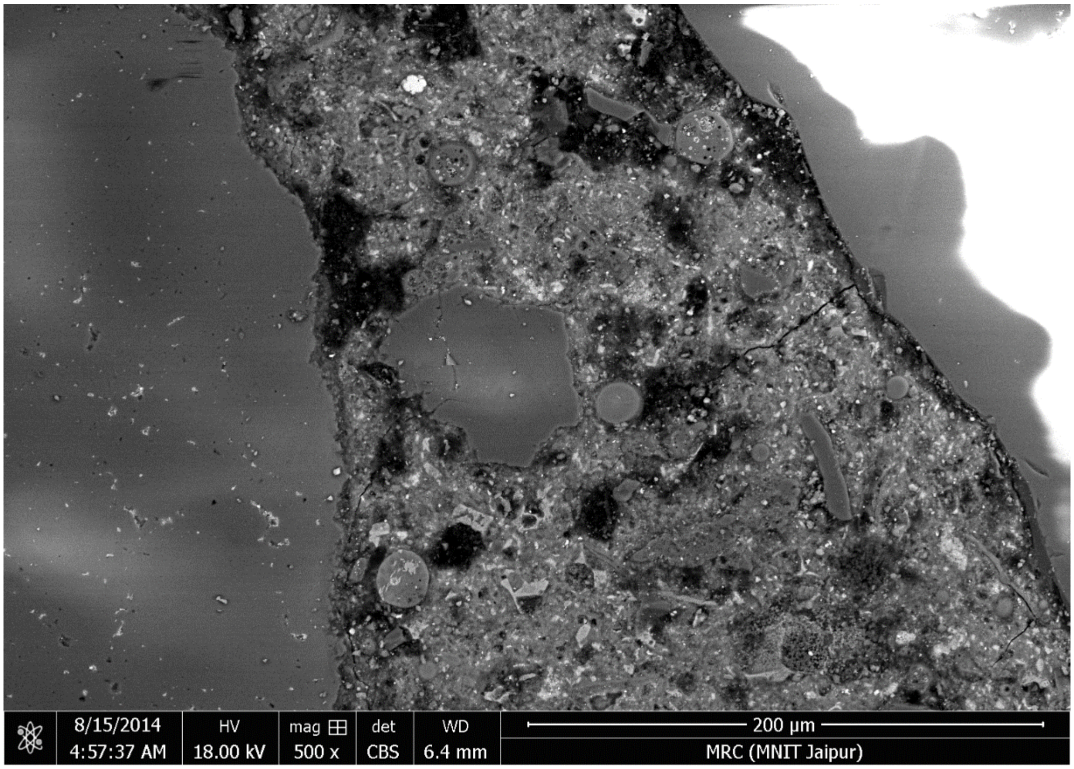


Figure 4.29 SEM Image of Concrete with W/C 0.50 & 25 % Jarosite (Series I)

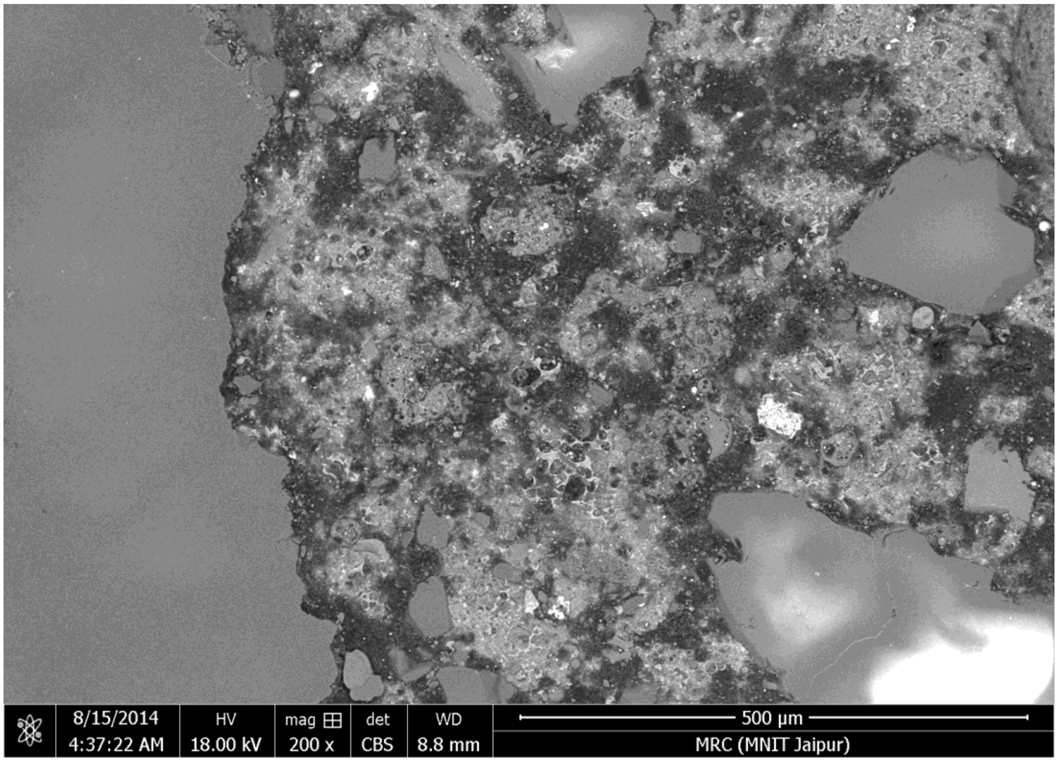


Figure 4.30 SEM Image of Control Concrete with W/C 0.40 (Series II)

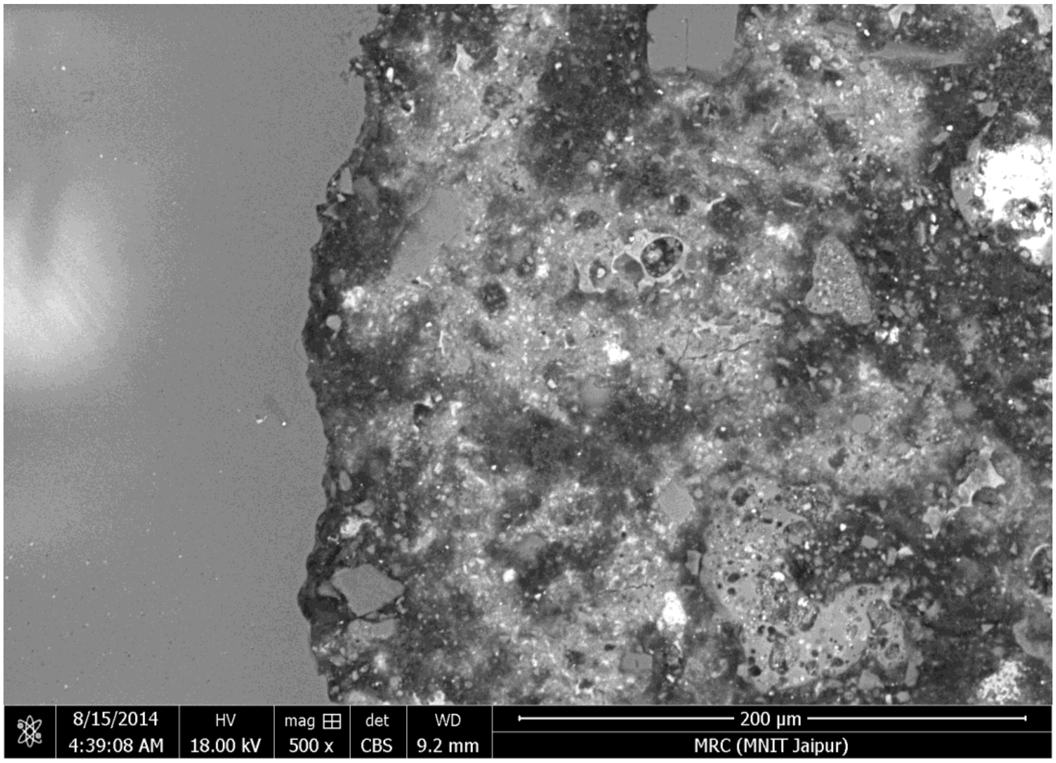


Figure 4.31 SEM Image of Concrete with W/C 0.40 & 5 % (Series II)

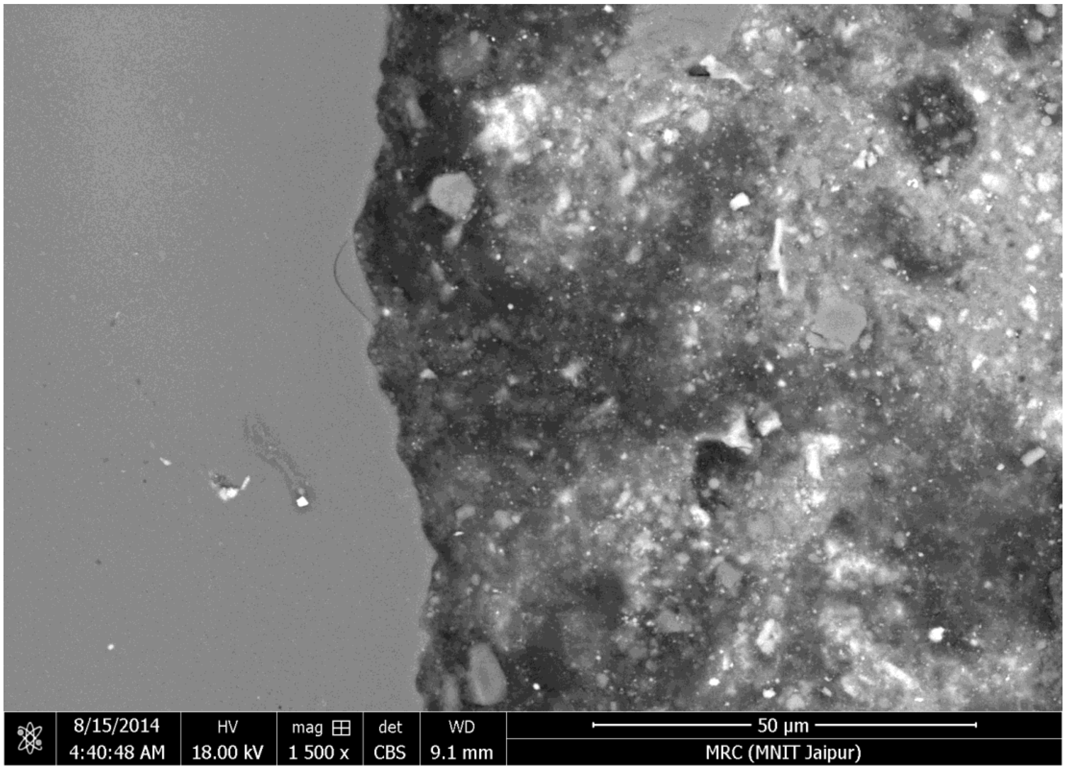


Figure 4.32 SEM Image of Concrete with W/C 0.40 & 25 % Jarosite (Series II)

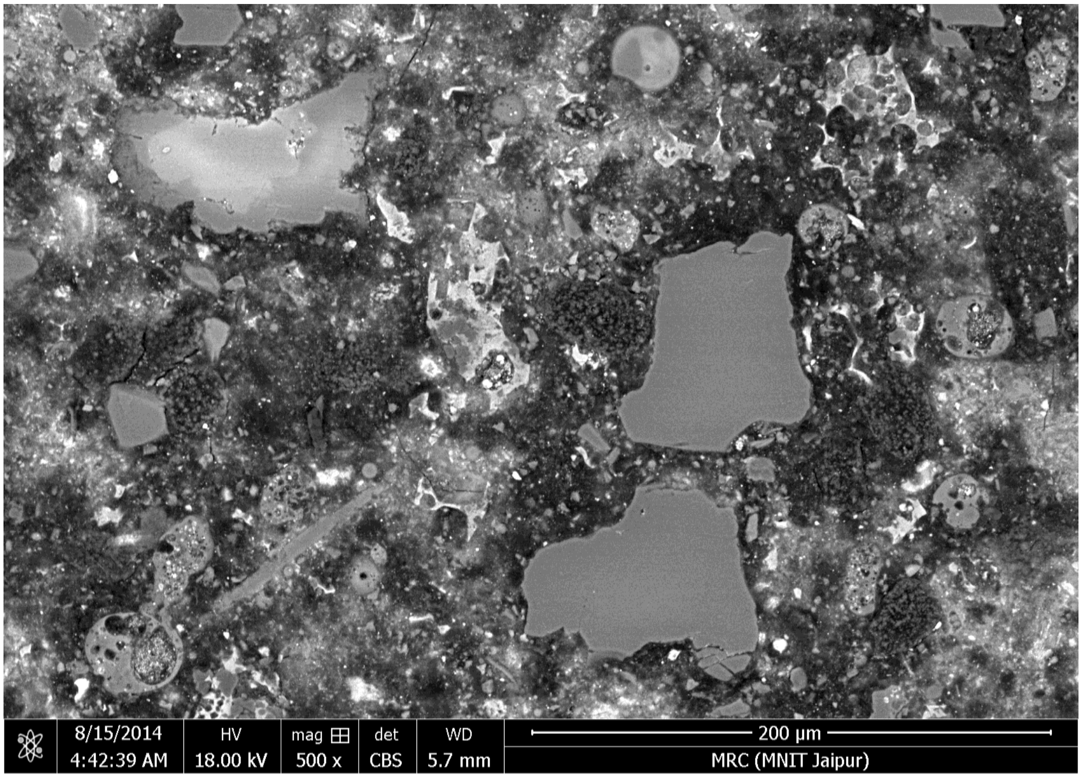


Figure 4.33 SEM Image of Concrete with W/C 0.45 & 5 % Jarosite (Series II)

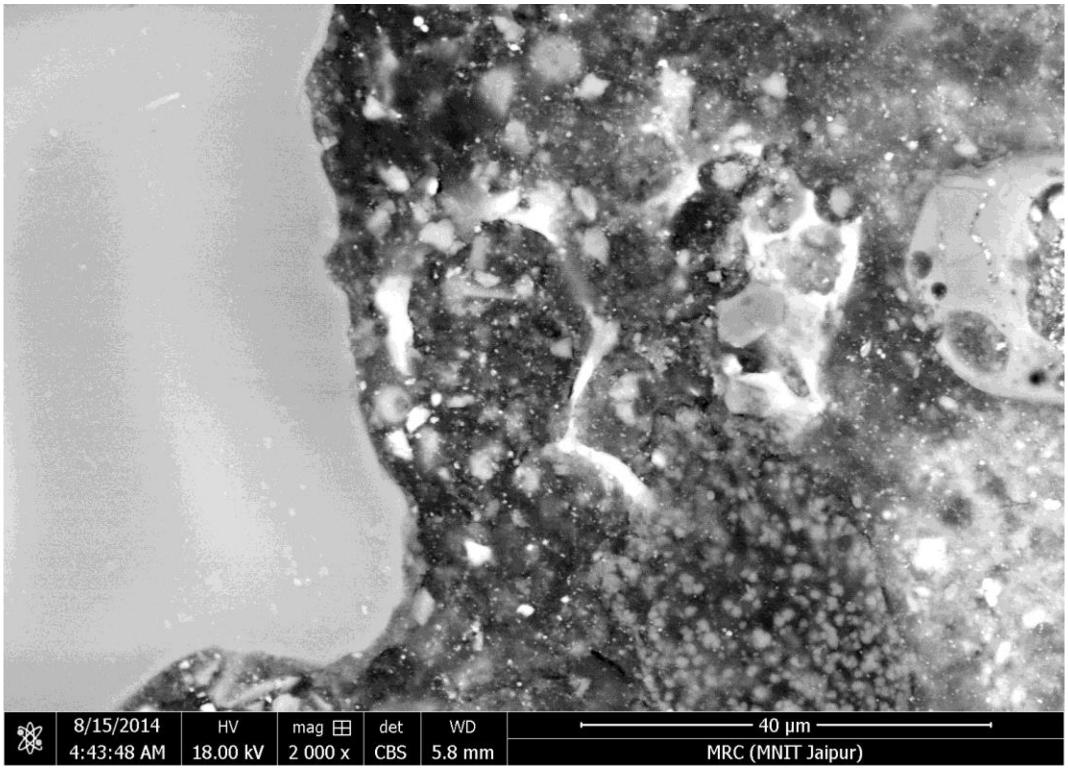


Figure 4.34 SEM Image of Concrete with W/C 0.45 & 25 % Jarosite (Series II)

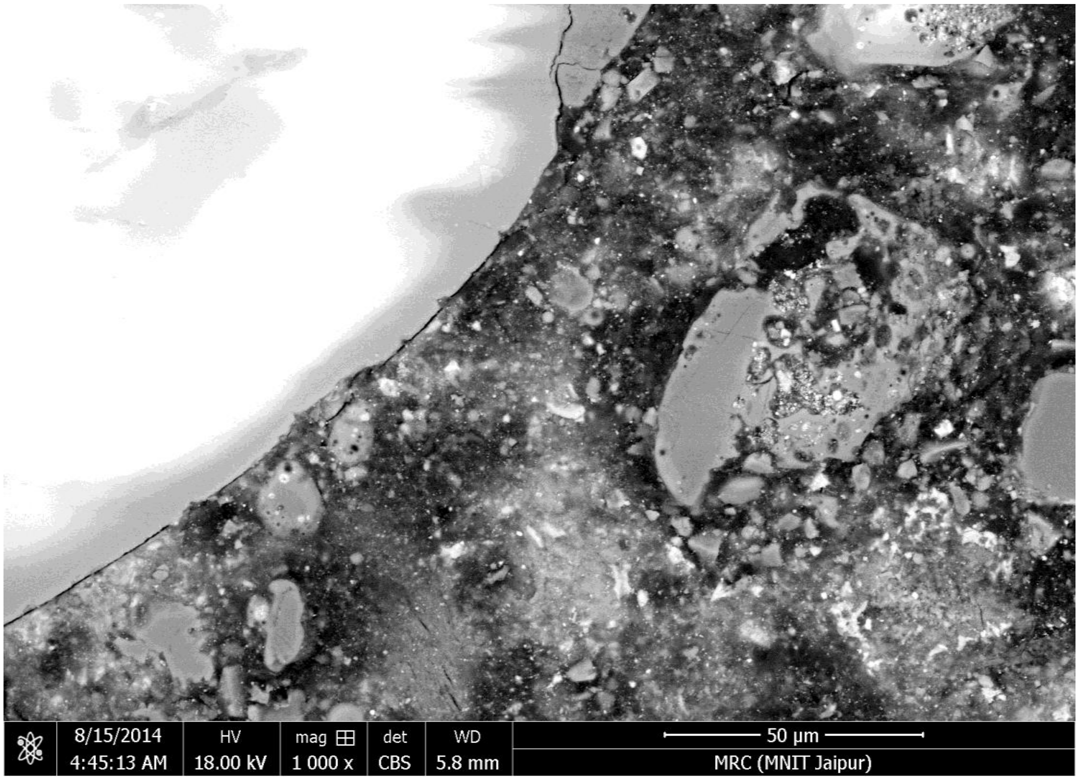


Figure 4.35 SEM Image of Concrete with W/C 0.50 & 5 % Jarosite (Series II)

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In series II, microscopic study visualizes wider cracks in specimen of concrete with 25 % jarosite and w/c 0.50. Other images has very fine lines (cracks) at ITZ.

4.12.2 XRAY DIFFRACTION

X-Ray diffraction for jarosite has been presented in figure 3.2. The XRay diffraction of Jarosite added concrete (w/c 0.45 & 25% jarosite) for series I & II has been graphed in Figure 4.36 & 4.37 respectively.

The jarosite diffraction showed the presence of dominating phase of Ammonium Iron Sulphate and Iron sulphate hydrate (Figure 3.2).

However, the X ray graph in figure 4.36 predicts the predominating phase SiO_2 and Calcium Silicate Hydrate in the concrete sample (Series I and II).

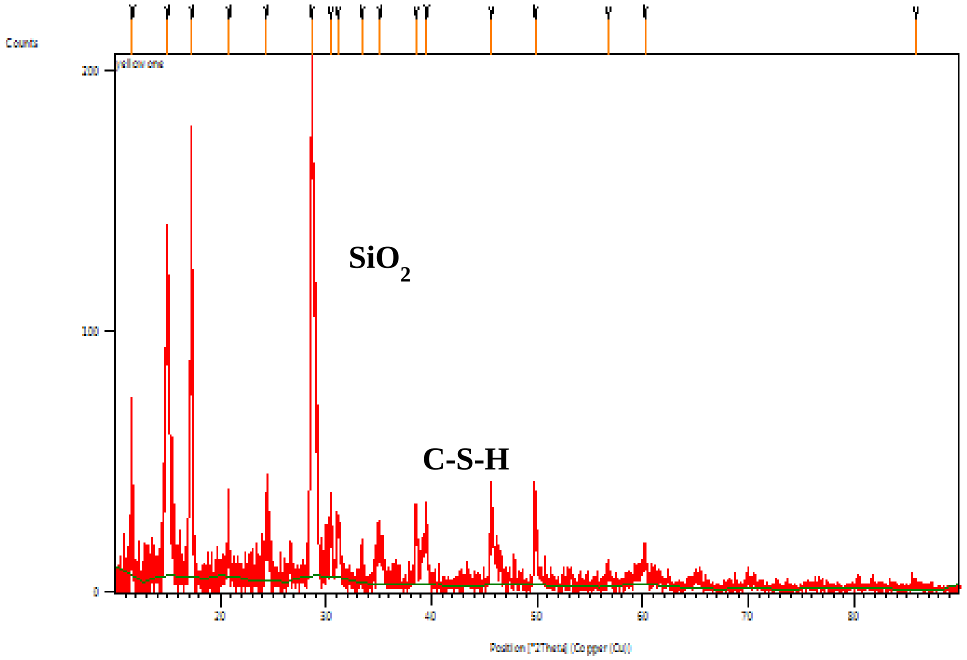

Figure 4.36 Xray diffraction of Jarosite added Concrete (Series I)

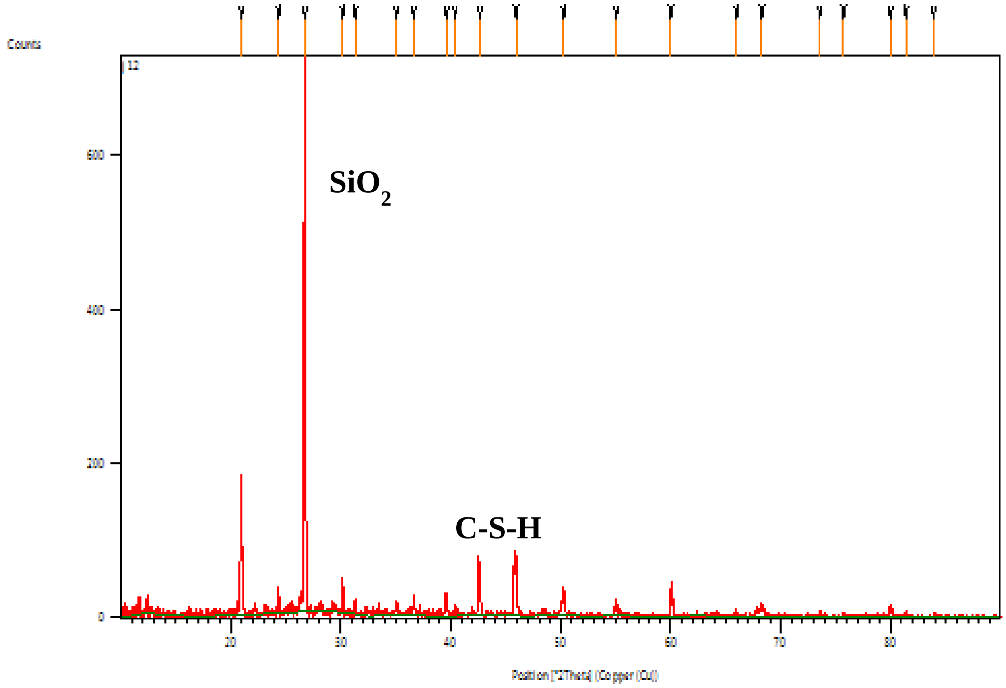

Figure 4.37 Xray diffraction of Jarosite added Concrete (Series II)

SUMMARY

S No	Property of Concrete	Result
1	Compressive Strength	Compressive strength decreases with increase in jarosite content in Series I. However, Strength improved in series II with higher jarosite content.
2	Flexural Strength	Flexural strength followed the similar trend of compressive strength.
3	Resistance to abrasion	Depth of wear in all the concrete mixtures were below the prescribed limit except for the specimen with w/c 0.45 and jarosite content 25%.
4	Water Permeability	In series I, jarosite concrete have high permeability and low & medium permeability have been experienced in concrete mixtures of Series II.
5	Water Absorption	In series I, lower absorption has been seen for concrete specimens with w/c 0.40 & 0.45 and increased absorption for specimens with w/c 0.50 at higher content of jarosite.
6	Water Sorptivity	Water sorption capacity increased with increased jarosite percentage in concrete (Series I) and decreased with increased jarosite percentage in concrete (Series II)
7	Chloride Ion diffusion	In series I, chloride diffusion increased when jarosite content increased. In series II, the chloride diffusion reduced with rise in jarosite content.
8	Chloride Ion Penetration	The chloride penetration increases with increase in jarosite content. Concrete samples in series II exhibited resistance to chloride ion penetration with higher jarosite content.
9	Carbonation	Maximum carbonated depth of 42 mm has been revealed in concrete with w/c 0.50 and 25% jarosite.
10	Corrosion	The results were satisfactory.
11	Sulphate Attack	No change in weight and strength (statistically) was found.
12	Toxicity leaching potential	Lead, Cadmium and Zinc in Raw powdered jarosite found to be more than prescribed limit as per USEPA. However, all the heavy elements (zinc, iron, lead, cadmium and copper) in jarosite added concrete were within the limits.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Jarosite was added in concrete as partial replacement of fine aggregate, with and without fly ash as a binder. Huge accumulation of jarosite waste has led to its disposal problem. The utilization of jarosite in concrete can resolves multifold issues of environment, ecology and sustainability. Following are the conclusions drawn:

Conclusions

1. The workability in terms of compaction factor for all the concrete mixtures has occurred in the range of 0.95-0.98, which can be regarded as quite a good workability.

2. The compressive and flexural strength of concrete mixtures has been almost higher at higher replacement levels at all w/c ratios. Good strength in fly ash-jarosite added concrete indicates the utility of jarosite for construction purposes.

3. The leaching test results seem favourable as well. The reduction in amount of heavy metals in concrete mixtures as compared to raw jarosite creates many ways of using jarosite for different purposes.

4. The durability properties in terms of water permeability (penetration, absorption and sorptivity), abrasion and carbonation has been within acceptable limits as per prescribed standards.

5. Chloride ion diffusion and penetration and corrosion to reinforcement of fly ash-jarosite added concrete has been appreciable.

6. Sulphate attack on concrete in 28 and 56 days had shown gradual loss of compressive strength. Lesser loss of strength in flyash-jarosite concrete at higher jarosite content seems favourable for construction under aggressive environment.

7. The SEM images and X ray diffraction graphs (Qualitative Analysis) has been evidence to support all the results for mechanical and durability properties.
8. Concrete mixtures with w/c 0.45 turns out to be more suitable for jarosite addition than other water-cement ratios.
9. Durable concrete can be made with jarosite as a partial replacement for natural fine aggregates & fly ash as binder and it could be applied in practical purposes.
10. Addition of jarosite as partial sand replacement in concrete (along with fly ash as mineral admixture) up to 25% could be a new alternative feasible solution to its disposal issue.

Future Recommendations

Reuse of jarosite as filler in concrete (along with fly ash as binder) has been well established in the study. However, the following parameters could be examined for future investigation.

1. The porosity for jarosite added concrete has not been tested and evaluated. The MIP (Mercury Intrusion Porosity) can be determined to analysis the structure for permeability purposes.

2. Quantitative analysis of X-ray diffraction needs to be performed for exact value of dominating phases in concrete.

3. Presence of Radioactive level in jarosite added concrete was not be evaluated in the present study and could be determined for construction use.

4. Shrinkage and freeze thaw effect on jarosite concrete need to study for using it in different climatic conditions.

5. Alkali Silica Reactivity of jarosite as a candidate to replace fine aggregates in concrete need to be address well. Due to laboratory limitations, the test cannot be performed in the present work and would highly recommended as a part of future research.

6. In the current study, Use of jarosite as replacement of fine aggregate in Concrete have been discussed. As an alternative solution to reduce the consumption of cement, use of jarosite as replacement of cement in Concrete could be a new research.

7. Different industrial wastes in combination with Jarosite can be studied for better mechanical and durability properties.

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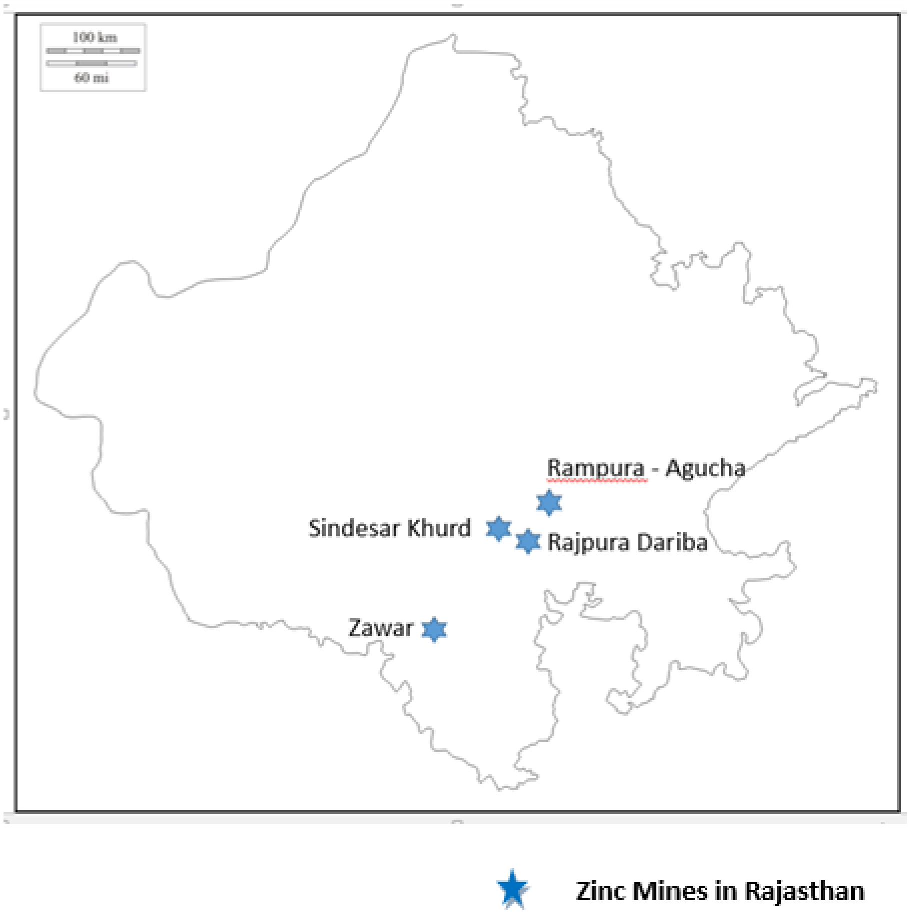
ANNEXURE: GIS Map showing Zinc Mines in State of Rajasthan



BIO-DATA

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Following is the list of the publications from the work.

JOURNALS

Mehra, P., Gupta, R., C., Thomas, B., S. (2016). "Properties of concrete containing jarosite as a partial substitute for fine aggregate". Journal of Cleaner Production, 120, 241-248.
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INTERNATIONAL CONFERENCES

Mehra, P., Gupta, R., C., Thomas, B., S., and Kumar. S. (2015). "Experimental And Analytical Studies on the Properties of Hazardous Jarosite Waste Added Concrete" In

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