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Assessment of Workability and Corrosion Characteristics of Copper Slag and Mineral Admixture Concrete

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Abstract: Copper slag is an industrial byproduct produced in large quantities by the process of manufacturing copper and Fly ash produced in huge volumes by the coal fired thermal power plants is being dumped on land adjoining their sites every year. Stockpiling of copper slag and fly ash on land is causing air pollution as well as land pollution to the beings. The present research was aimed to evaluate the Copper slag which has been proposed as an alternative to river sand that gives additional benefit to concrete. The objective of this work is to study the strength and corrosion resistive properties of concrete containing copper slag as fine aggregate (0% to 100%) along with fly ash (0% to 30%) by weight of cement. Consumption of copper slag and fly ash in the manufacturing of concrete will nearby is cost-effective as well as environmental way of their disposal in conserving the natural resources. The results of mechanical properties of concrete in incorporating copper slag and fly ash were hopeful. Assessment of slump aspects of concrete incorporating copper slag as a sand and fly ash as a cement replacement is as important as the mechanical properties. In this study compressive strength and durability aspects of concrete such as ultrasonic pulse velocity, rapid chloride penetration, and by Rapid Chloride Penetration performance laboratory test. The test results indicate that copper slag and fly ash in concrete give you an idea about better dimensional performance, slightly better resistance to Water absorption test as compared to conventional concrete. No weight loss and reduction in compressive strength in concrete samples made from copper slag that is immersed in Chloride solution under observance. After 28, 60, 90 days of immersion in 5% magnesium Chloride solution, Copper slag concrete showed better resistance to chloride ion penetration. The optimum percentage addition of the fly ash by weight of cement in concrete containing copper slag as fine aggregate was also determined.

Keywords: *Copper Slag, Fly Ash, Slump, Compressive strength, Ultrasonic pulse velocity, Water absorption test, Rapid Chloride Penetration.*

1. Introduction

In the separation of copper, slag is a by-product obtained during the matte smelting and refining of copper has been reported by Biswas and Davenport (2002). The major constituent of a smelting charge are sulphides and oxides of iron and copper. The charge also contains oxides such as SiO_2, Al_2O_3 CaO and MgO, which are either present in original concentrate or added as flux. It is Iron, Copper, Sulphur, Oxygen and their oxides which largely control the chemistry and physical constitution of smelting system. The main reason for the premature failure of reinforced concrete structures is corrosion of the reinforcements. The use of new mortars based on ternary mixtures, an alternative to ordinary Portland cement (OPC), requires extensive research in order to check its passivizing properties for reinforcements and the instability or permanence of the passive state achieved. Pozzolonas and slag extends the market for concrete by improving specific properties of concrete products, allowing them to be constructed with other materials or placed in environments that would have precluded the use of Portland cement alone. In properly formulated concrete mixtures, Pozzolonas and slag have been shown to enhance long-term strength, decreased permeability, increased durability, and reduction in thermal cracking of bulk concrete. The workability of concrete reduces due to the free flow of water left in the concrete due to less absorption of water by copper slag. On 50% replacement of copper slag, it also gives more strength than conventional concrete Arivalagan. S, (2013).

An experimental investigation was conducted on the properties of concrete to study the effect of using copper slag as a fine aggregate. There was more than 70% improvement in the compressive strength of mortar with 50% copper slag substitution in comparison with the control mixture. The volume of permeable voids decreased with the replacement of up to 50% copper slag Khalifa S. Al-Jabri (2011). This work reports an experimental procedure to investigate the effect of using copper slag as partial replacement of sand. The result indicated that workability increases with increase in copper slag percentage. The highest compressive strength obtained was 46Mpa (for 100% replacement) and the corresponding strength for control mix was 30Mpa Meenakshi Sundarvizhi. S (2011).

High performance concrete should be designed to have the advanced workability and better durability than those of conventional concretes. Thus this research was performed to evaluate the potential use of copper slag as sand replacement in the production of high performance concrete D. Brindha, S. Nagan, (2010). This research study was conducted to investigate the performance of high strength concrete (HSC) made with copper slag as a fine aggregate. The result shows that the water demand was reduced by almost 22% at 100% copper slag replacement compared to the control mixture .Khalifa S.Al-Jabri et al (2009).

Investigated the effect of using copper slag as a replacement of sand on the properties of high performance concrete (HPC). Concrete mixtures were prepared with different proportions of copper slag ranging from 0% (for the control mix) to 100%. Addition of up to 50% of copper slag as sand replacement yielded comparable strength with that of the control mix. However, further additions of copper slag caused reduction in the strength due to an increase of the free water content in the mix Al-Jabri (2009).

Copper slag is also used as fine aggregate in the design of bituminous concrete and semi dense bituminous concrete, which increases the property of the bituminous mixes Gorai, B., Jana, R.K. and Premchand, M (2003). Thus this study focused on the effect of copper slag by surrogating fine aggregate in M35 grade Portland Pozzolona cement concrete and they were cured for 7 days, 28 days, 60 days and 90 days. Then the obtained results were compared with the conventional concrete made using Portland Pozzolona cement. Reinforced concrete structures are exposed to harsh environments yet is often expected to last with little or no repair or maintenance for long periods of time (often 100 years or more). To do this, a durable structure needs to be produced. For reinforced concrete bridges, one of the major forms of environmental attack is chloride ingress, which leads to corrosion of the reinforcing steel and a subsequent reduction in the strength, serviceability, and aesthetics of the structure. The different mechanisms of chloride penetration are presented, followed by a further elaboration of the chloride diffusion theory.

The influence of basic properties of concrete on its chloride penetrability is also discussed. Chloride penetration of concrete pavement structures is determined through the Rapid Chloride Permeability test (RCPT), which typically measures the number of coulombs passing through a concrete sample over a period of six hours at a concrete age of 7, 28, and 56 days. In a composite material, such as concrete, the parameters of the mixture design and interaction between them determine the behaviour of the material.

The rate of ingress of chlorides into concrete depends on the pore structure of the concrete, which is affected by factors including materials, construction practices, and age. The penetrability of concrete is obviously related to the pore structure of the cement paste matrix. This will be influenced by the water-cement ratio of the concrete, the inclusion of supplementary cementing materials which serve to subdivide the pore structure McGrath, 1996, and the degree of hydration of the concrete. The older the concrete, the greater amount of hydration that has occurred and thus the more highly developed will be the pore structure. This is especially true for concrete containing slower reacting supplementary cementing materials such as fly ash that require a longer time to hydrate Tang and Nilsson, 1992; Bam forth, 1995. Because these conductors influence the results so that a higher coulomb value than would otherwise be recorded is determined, the method still could serve as a quality control test. It can qualify a mix, but not necessarily disqualify it Ozyildirim, 1994. Chloride permeability is an inherent property of concrete and needs to be assessed independently for long term durability, especially in the design and construction of structures to be built in a salt-laden environment. Wherever there is a potential risk of chloride-induced corrosion, the concrete should be evaluated for chloride permeability Joshi and Chan, (2002).

2. Materials and Properties

2.1. Cement

The cement used in this project is Ordinary Portland Cement of 43 Grade from Ultratech Cement Company. This cement is most widely used in the construction industry in India.

2.2. Coarse and Fine Aggregate

Coarse aggregate of 20mm size and fine aggregate of zone III from Karur area of Tamil Nadu

2.3. Copper Slag

The slag is a black glassy granular material, by product of Sterlite Industries Limited (SIL), Tuticorin, Tamil Nadu, India.

2.4. Fly Ash

Fly ash of class C is obtained from thermal power plant, Mettur, TamilNadu, India was used.

3. Physical and Chemical Properties

3.1. Physical properties of OPC and Fly ash

Ordinary Portland cement from Ultratech Cement Company is used for super grade. The cement is produced as per the IS (Indian standard) specification given in IS: 1489 Part-I-1991.Fly ash of class C is obtained from thermal power plant. IS: 3812 Part-I - 2003

The Physical properties of Ordinary Portland Cement and Fly ash are given in Table 3.1

Table 3.1 *Physical properties of OPC and Fly ash*

S. No	Physical Properties	OPC	Fly ash
1.	Fineness modulus	335.7 m^2/kg	397 m^2/kg
2.	Initial setting time	28 min	130 min
3.	Final setting time	595 min	290 min
4.	Soundness	0.8%	0.20%
5.	Specific gravity	3.15	2.14

3.2. Chemical properties of OPC and Fly ash

The Chemical properties of Ordinary Portland Cement and Fly ash are given in Table 3.2

Table 3.2 *Chemical properties of OPC and Fly ash*

Component	OPC (%)	Fly ash (%)
Silica (sio_2)	20.85	58.65
Alumina (Al_2SO_3)	4.78	15.65
Iron oxide (Fe_2O_3)	3.51	6.08
Calcium oxide (CaO)	63.06	3.50
Magnesium oxide (MgO)	2.32	0.28
Sulfuric trioxide (SO_3)	2.48	0.16

3.3. Chemical Components of Copper Slag

The Chemical components of Copper Slag are given in Table 3.3

Table 3.3 *Chemical components of Copper Slag*

Component	CS (%)
Silica (sio_2)	33.05
Alumina (Al_2so_3)	2.79
Iron oxide (Fe_2o_3)	53.45
Calcium oxide (Cao)	6.06
Magnesium oxide (MgO)	1.56
Sulfuric trioxide (so_3)	1.89

3.4. Various Replacements of Copper Slag and Fly Ash in Concrete

The various replacements of Copper slag and Fly ash are given in Table 3.4

Table 3.4 *Replacement of Copper slag and Fly ash*

S.NO	Cement (%)	Fly ash (%)	FA (%)	CS (%)
1.	100	0	100	0
2.	70	30	90	10
3.	70	30	80	20
4.	70	30	70	30
5.	70	30	60	40
6.	70	30	50	50
7.	70	30	40	60
8.	70	30	20	80
9.	70	30	0	100

4. Testing of Materials

4.1. Sieve Analysis

The sample of aggregate was split into various fractions, each consisting of particles of the same size. The sieve analysis is conducted to determine the particle size distribution in a sample of aggregate. The aggregate used for making concrete are 4.75mm, 2.36mm, 1.18mm, 600 micron, 300 micron, and 150 micron. The aggregate passes through 40mm and retained at 4.75mm as coarse aggregate and the aggregate passes through 4.75mm and retained at 150 micron as fine aggregate. Sieve can be done manually or mechanically.

From the below Fig.4.1, it is unstated that the fineness modulus of copper slag (3.76) is more than the fineness modulus of fine aggregate (2.73).Thus, the copper slag can be used as fine aggregate in concrete.

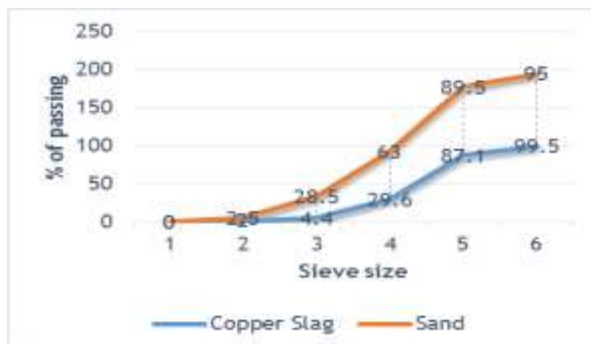

Fig.4.1 *Sieve Analysis*

4.2. Specific Gravity

The Specific gravity of aggregate is made use of in design calculation of concrete mixes. The specific gravity is calculated as the ratio between the weight of a given volume of the material and weight of an equal volume of standard material. Specific gravity of aggregate is required in calculating the factor in connection with the workability measurements. The Specific gravity of materials are given in Table 4.1

Table 4.1 *Specific gravity of materials*

S.No	Material	Specific gravity
1.	Cement	3.15
2.	Fly ash	2.14
3.	Fine aggregate	2.65
4.	Copper Slag	3.91
5.	Coarse aggregate	2.64

5. Tests on Fresh Concrete

5.1. Slump Test

Slump test is the most commonly used method of measuring the consistency of concrete. A concrete is said to be workable if it can be easily mixed and easily placed, compacted and finished. These results in large voids, less durability and less strength. The increase in water cement ratio increases the slump and workability but decreases the strength of concrete.

From the below Fig.5.1 shows the workability of concrete as Slump value.

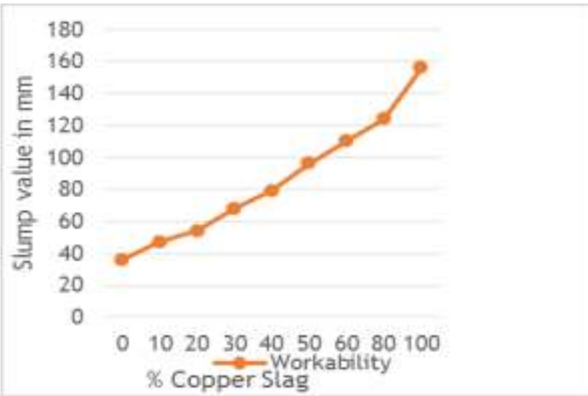

Fig.5.1 *Workability of concrete*

6. Tests on Hardened Concrete

6.1. Compression Test

In order to determine the compressive strength cube mould of size 150×150×150 mm were casted. The cubes were casted for different percentage of copper slag from 0% to 100%. The mould is cleaned and oiled properly along its faces. Then the concrete is compacted properly using tamping rod. Then the cubes are kept curing for 7day,28 day,60 day and 90 day. The compression test is done according to the specification IS 516:1959. The compressive strength is calculated using the formula

Compressive strength =P/A

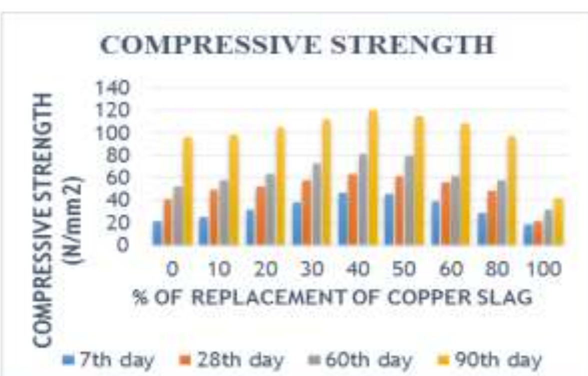

Fig.6.1 *Replacement % Vs Compressive Strength*

From the above fig 6.1 it is known that in the 7th day testing the compressive strength is maximum at 40% on surrogating fine aggregate by copper slag which is about 46.98 N/mm^2 where the conventional concrete having compressive strength of 21.62N/mm^2 . On 28th day testing the compressive strength 63.54N/mm^2 by surrogating 40% of fine aggregate were the conventional concrete contain compressive of about 41.33N/mm^2 . On 60th day compressive testing it is also found that the maximum strength is 40% (81.68 N/mm^2) surrogating fine aggregate. Whereas on 90th day compressive testing the maximum strength is at 40% (119.65 N/mm^2) surrogating fine aggregate.

6.2. Split Tensile Test

For testing split tensile strength concrete cylinder of size 150 mm diameter and 300mm height were casted with different percentage of copper slag. The mould where properly cleaned and oiled then the concrete is filled in three layer then each layer is compacted using tamping rod. It is cured for 7, 28, 60 and 90 days. The load is applied until the failure occurs and failure lode is noted. The split tensile strength is calculated using the formula

Split tensile strength=2P/πLD

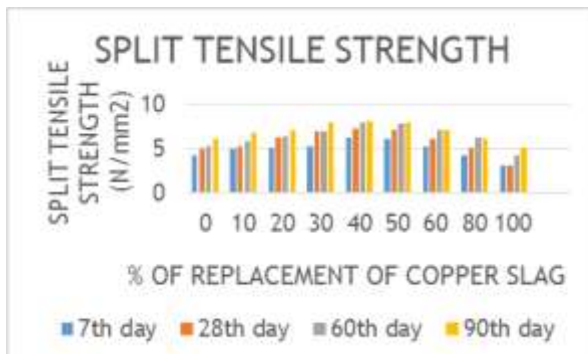

Fig 6.2.1 *Replacement % Vs Split Tensile Strength*

From the fig 6.2 the split tensile strength of concrete with 40% surrogating fine aggregate by copper slag has the maximum split tensile strength. In that 7th day, 28th day, 60th day and 90th day. On surrogate concrete the 7th day split tensile strength is 6.24 N/mm^2 where the conventional concrete is about 4.23 N/mm^2. In 28th day it is about 7.25 N/mm2 where conventional concrete is about 4.89 N/mm^2. In 60th and 90th day it is about 7.89 N/mm^2 and 8.06 N/mm^2 where the conventional concrete is 5.29 N/mm^2 6.02 N/mm^2. 3.6. Flexural strength on reinforced concrete beam Reinforced concrete beams are typically used in framed structures. Flexural strength, also known as modulus of rupture, bend strength, or fracture strength a mechanical parameter for brittle material, is defined as a material's ability to resist deformation under load. The transverse bending test is most frequently employed, in which a rod specimen having either a circular or rectangular cross-section is bent until fracture using a three point flexural test technique. Tests were carried out on reinforced concrete beam specimens of size 1100mm x 100mm x 150mm shown in fig 3.3. Testing was carried out in the UTM (Universal Testing Machine). The tested beams were instrumented to measure the applied load, deflection along the beam span, strains at the mid span. Both side surfaces of the beam were painted in white colour with the objective of observing the crack development during testing. The load was kept constant while cracks were marked and photographed. The inclined crack width at load points or supports and corners of the opening was monitored. The deflections were measured using dial gauge in mid span and under the load point. Dial gauge having sensitivity of 0.01mm was used to trace the deflection profile of the beam by placing along the center line of the beam. The average modulus of rupture (flexural strength) was determined using the following expression.

$$F_{cr} = \frac{PL}{BD^2}$$

Where,

F_{cr}= Modulus of rupture
P= Ultimate load in KN
L= Length of beam in mm
B= Width of specimen in mm
D= Depth of specimen in mm

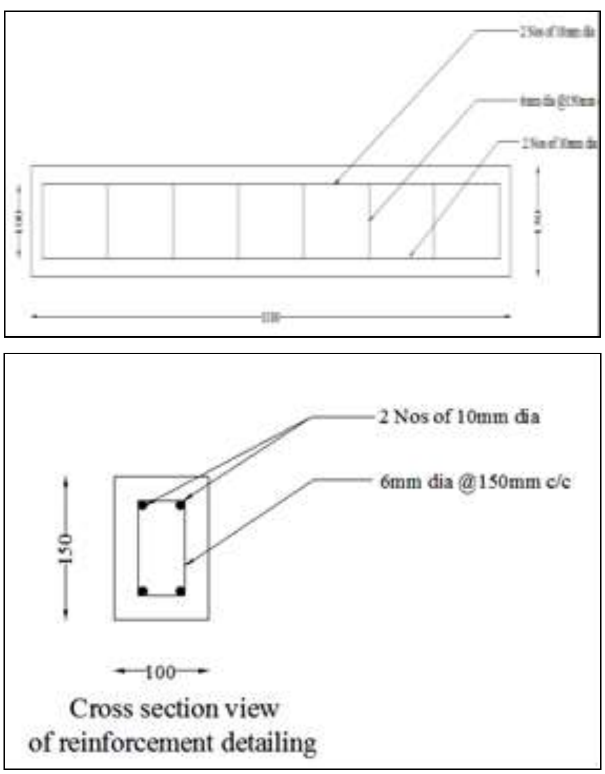

Fig 6.2.2 *Reinforcement details*

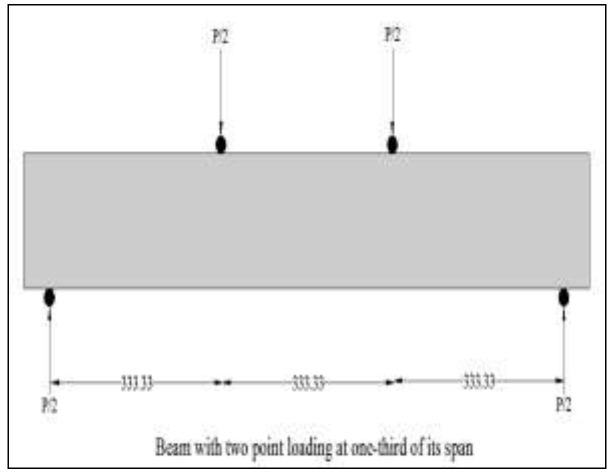

Fig.6.2.3. *Experimental setup*

The flexural strength tests were carried out for 28 days. For each concrete mixture, 1100 x 100 x 150mm beams were casted for conventional and for optimum replacement percentage, improved mechanical properties compared to nominal concrete mixture. The graph plotted against load versus deflection is shown. The load deflection curve indicates that the concrete specimens replaced with copper slag are withstanding with higher loads.

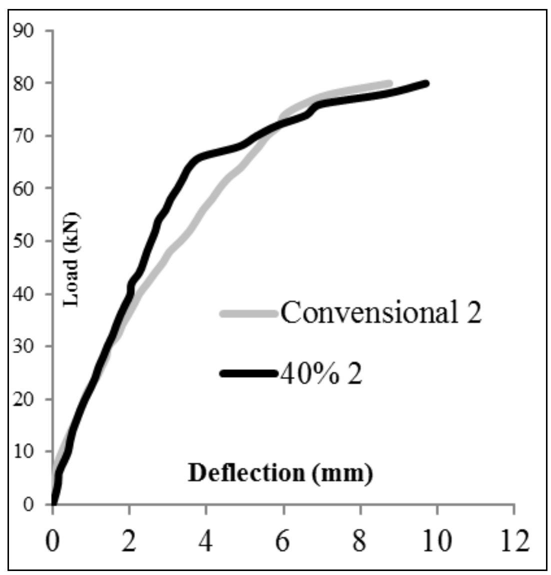

Fig.6.2.4 *load vs. deflection*

6.3. Ductility

Ductility of reinforced structures is a desirable property where resistance to brittle failure during flexure is required to ensure structural integrity. Ductile behavior in a structure can be achieved through the use of plastic hinges positioned at appropriate locations throughout the structural frame. These are designed to provide sufficient ductility to resist structural collapse after the yield strength of the material has been achieved. The available ductility of plastic hinges in reinforced concrete is determined based on the shape of the moment-curvature relations. Theoretical moment-curvature analysis for reinforced concrete structural elements indicating the available flexural strength and ductility can be constructed providing that the stress-strain relations for both concrete and steel are known. Moment-curvature relationship can be obtained from curvature and the bending moment of the section for a given load increased to failure. The ductility factor for various beams are shown in T and Fig.6.3.2

$$\mu = \frac{\delta_u}{\delta_y}$$

Where,

μ= Ductility factor

δ_u = Deflection corresponding to $0.8\,P_u$

δ_y = Deflection corresponding to P_y

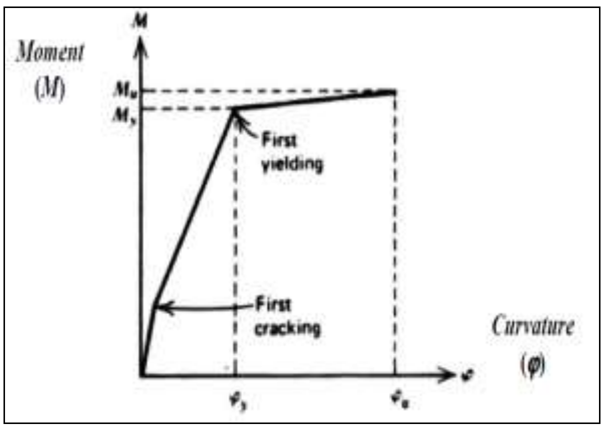

Fig.6.3.1 *Trilinear moment-curvature relationship*

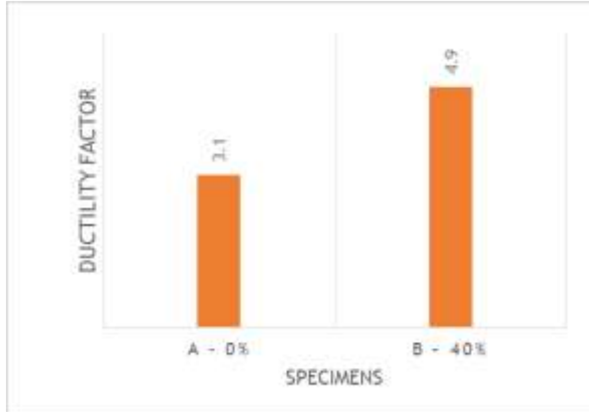

Fig.6.3.2. *Ductility factor*

6.4. Ultrasonic Pulse Velocity Test

A reference bar is provided to check whether the instrument is zero initially. The pulse time for the bar is marked on it. Apply a smear of grease to the transduced faces before placing it on the opposite ends of the bar. Adjust the SET REF control until the reference bar transit time is obtained on the instrument read out. For maximum accuracy, it is recommended that the 0.1 micro second range be selected for path length up to 400mm. Having determined the most suitable test points on the material to be tested make careful measurement of the path length 'L'. Apply car plant to the surface of the transducers and press it hard on to the surface of the material. Do not move the transducers while reading is taken as this can generate noise signals and error in measurements. Continuous holding of the transducers onto the surface of the material, until a constant reading appears on the display .It is the time in microsecond for the ultrasonic pulse to travel the distance L. The mean value of the display readings should be taken when the unit digit hunts between the two values.

$$\text{Pulse velocity} = \frac{\text{Path length}}{\text{Travel time}}$$

The ultrasonic pulse velocity of the hardened concrete values are given in the below Table 6.4.

Table 6.4 *Ultrasonic pulse velocity of concrete*

S. No	Replacement % of copper slag in concrete	Replacement % of fly ash in concrete	Distance in (mm)	Transmit time (μsec)	Pulse velocity in (KN/sec)	Concrete quality
1	C_C S (0%)	Cc (0%)	150	32.20	4.615	Excellent
2	CS10	Fly ash 30%	150	30.80	4.870	Excellent
3	CS 20	FA 30%	150	30.50	4.747	Excellent
4	CS30	FA 30%	150	31.60	4.870	Excellent
5	CS40	FA 30%	150	34.10	5.208	Excellent
6	CS50	FA 30%	150	33.40	4.491	Excellent
7	CS60	FA 30%	150	32.20	4.615	Excellent
8	CS80	FA 30%	150	30.70	4.886	Excellent
9	CS100	FA 30%	150	29.80	5.208	Excellent

6.5. Water Absorption Test

The full size blocks shall be completely immersed in clean water at room temperature for 24 hours. Then the blocks are removed from the water and allowed to drain for one minute by placing them on a 10mm or coarse wire visible surface mesh and dried blocks weighed immediately .After weighing, all blocks shall be dried in a ventilated oven at 100 to 1150^{0}c for not less than 24 hours and then two successive weighing are taken at an intervals of 2 hours shows an increment of loss of not greater than 0.2 percent of the last previously determined mass of the specimen.

The absorption percent $= \frac{A-B}{B}$ **x 100**

Table 6.5 *Results for Water Absorption Test*

S. No	Mix id		Weight of saturated specimens (Kg)	Weight of oven dried specimens (Kg)	Saturated water absorption @ 56 days (%)
1	CC	Fly ash (0%)	8.6	8.4	2.3
2	S10	FA 30%	8.74	8.6	2.2
3	S20	FA 30%	8.87	8.7	2.1
4	S30	FA 30%	8.92	8.79	1.9
5	S40	FA 30%	9.04	8.88	1.8
6	S50	FA 30%	9.26	8.90	3.2
7	S60	FA 30%	9.48	8.95	3.0
8	S80	FA 30%	9.53	8.76	2.7
9	S100	FA 30%	9.76	8.69	3.1

6.6. Rapid Chloride Penetration Test

Chlorides penetrate through crack-free concrete by a variety of mechanisms: capillary absorption, hydrostatic pressure, diffusion and evaporative transport. Of these, diffusion is predominant. Diffusion occurs when the concentration of chloride on the outside of the concrete member is greater than inside. This results in chloride ions moving through the concrete to the level of the rebar. When this occurs in combination with wetting and drying cycles and in the presence of oxygen, conditions are right for reinforcement corrosion.

Concrete disc specimens of size 100mm diameter and 50mm thick were cast for various replacement percentages of sand and cement with copper slag and fly ash in concrete. After 24 hours, the disc specimens were removed from the mould and subjected to curing for 90 days in chloride free distilled water. After curing, the specimens were tested for chloride permeability. All the specimens were dried free of moisture before testing.

The test involves obtaining 100 mm (4 in.) diameter core of cylinder sample from the concrete being tested. A 50 mm (2 in.) specimen is cut from the sample. The side of the cylindrical specimen is coated with epoxy. When the epoxy is dried, it is put in a vacuum chamber for 3 hours. The specimen is saturated with vacuum for 1 hour and allowed to soak for 18 hours. It is then placed in the test device (see test method for schematic of device). The left-hand side (–) of the test cell is filled with a 3% NaCl solution. The right-hand side (+) of the test cell is filled with 0.3N NaOH solution. The system is then connected and a 60-volt potential is applied for 6 hours. Readings are taken for every 30 minutes. At the end of 6 hours, the sample is removed from the cell and the amount of coulombs passed through the specimen is calculated.

Table 6.6 *Rapid Chloride Penetration Test*

Mix (%)	Charge passed in Coulombs	As per ASTM C1202 Chloride penetrating rate
CC	623.89	Very low
CS10+FA30	913.62	Very low
CS20+FA30	1033.01	Low
CS30+FA30	1210.35	Low
CS40+FA30	1487.47	Low
CS50+FA30	1700.31	Low
CS60+FA30	1901.42	Low
CS70+FA30	2053.33	Moderate
CS80+FA30	2144.76	Moderate
CS100+ FA30	2389.95	Moderate

7. Conclusion

1. From the test results, it has been founded that the average pulse velocity is above 5 km/sec for 40% copper slag replacement with fine aggregate and 30% replacement with cement.
2. The sieve analysis test proves that the copper slag can be surrogated for fine aggregate in concrete.
3. Water absorption in replaced concrete is lower than the conventional concrete.
4. Rapid Chloride Penetration in replaced concrete is lower than the conventional concrete.
5. As the subrogation of copper slag increases, the workability of concrete decreases because of free water left in the concrete.
6. The compressive strength on concrete is found to be increased by surrogating fine aggregate with 40% of copper slag.

7. By surrogating 40% of fine aggregate by copper slag, the split tensile strength is increased.
8. It has been understood that for a 40% replacement, the density of the mix becomes high and free from pores.
9. Up to 40% replacement of copper slag with fine aggregate showed very less water absorption than conventional concrete.
10. Beyond 40%, the segregation and bleeding effect of copper slag and fly ash mixed concrete increases, thereby increasing value of water absorption.
11. Finally this overall review concluded that the effect of different kinds of industrial waste in concrete properties like slump value, workability, mechanical properties of hardened specimen and durability were studied. This paper will also encourage the utilization of copper slag and fly ash derived from various industries.

8. Acknowledgements

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