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Resistance of Geopolymer Concrete Against Sodium Sulfate (Na_2SO_4) Solution

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Abstract- **Deterioration of Concrete structures in sulfate environment is a fully noted fact. Sulfate resistance of the blend greatly depends on the cement chemistry, and also on the chemistry of the pozzolan used and its replacement level.**
This research presents the experimental investigation done on the performance of Rice Husk Ash, and Waste Paper Ash Concrete subjected to severe environmental conditions. Rice Husk Ash and Waste Paper Ash were used as supplementary cementing material in cement mortars to evaluate sulfate resistance in sodium sulfate solution. The concrete specimens were cured in both normal and sulfate water for 7 and 28 days. The cement (OPC of grade 43) was replaced by Rice Husk Ash, and Waste Paper Ash in the range of 5% to 15% by weight and also by the Mix (Rice Husk Ash+Waste Paper Ash) up to 10% by weight for M20 mix. The slump, compressive strength, split tensile strength, flexural strength, permeability, and the weight loss of the mortar mixed with Rice Husk Ash and Waste Paper Ash were examined and compared with that of the control concrete for both the normal and sulfate water environment. It was found that compressive strength, split tensile strength, and the flexural strength increased **at 5% and 10% replacement with Rice Husk Ash, Waste Paper Ash, and Mix and also, 10% Waste Paper Ash concrete was having the highest strength. During sulfate water environment, the strengths increased up to 15% replacement with Rice Husk Ash, and Waste Paper Ash but compared to normal environment it was less. There was a considerable decrease in the workability as the percentage of Rice Husk Ash, and Waste Paper Ash was increased. The Rice Husk Ash concrete and Waste Paper Ash concrete was found to be less permeable than the control concrete. There was not much effect on the weight of the concrete specimens during the normal water environment, however, there was a significant effect on the weight during the sulfate water environment. The results also showed that the Rice Husk Ash Concrete, Waste Paper Ash Concrete and Mix (Rice Husk Ash+Waste Paper Ash) Concrete gives the less loss of strength than the Control Concrete at all the percentages of replacement.**

Key words: Rice husk ash (RHA), Waste paper ash (WPA), Compressive strength, Flexural strength, Split tensile strength, Workability, Durability, Sulfate Attack, Grade of concrete (M20)

1. INTRODUCTION

Sulfate attack is the most assertive environmental atrophy that disturbs the long period strength and durability of concrete constructions. The sulfate attack of concrete structures leads to severe premature deteriorations (Kalousek et al. 1972; Vladimir 1987). Sulfates are naturally present in weighty amounts in soil, ground water, industrial effluents, and wastes from chemical and mining industries, and sea water, and are also present internally in concrete structures due to the use of sulfate rich aggregates, cement containing excess gypsum, and sulfate bearing water.

Solid sulfates do not attack the concrete severely but when other chemicals come into contact, they try to find entry into porous concrete and react with the hydrated cement products (K. Nirmalkumar and V. Sivakumar (2008)). The sulfate ions in the solution, which come from any of the previously mentioned sources are found in combination with other ions such as sodium, potassium, magnesium, and calcium. The sulfate ions react with C_3A and $Ca(OH)_2$, which gives rise to expansive and softening types of deteriorations (Ramezanianpour et al. (2012)).

The mechanism of attack of sodium sulfate on the concrete construction is mainly due to the two principal reactions, which give rise to the expansive ettringite, and gypsum. First is the reaction of sodium sulfate (Na_2SO_4) with the calcium hydroxide produced from cement hydration to form gypsum, and second is the reaction of the formed gypsum and the calcium aluminate hydrates to form ettringite (Santhanam et al. (2002, 2003), Ramezanianpour et al. (2012)).. The formation of gypsum and ettringite leads to expansion, cracking, deterioration, and disruption of concrete structures. These two out products are having the volume much higher than that of the solid reactants, as a consequence stresses are produced in the concrete, that may result in the weakening of the paste and ultimately in the premature failure of concrete (Venkatanarayanan et al. (2014)). Thus, the sulfate resistance of the concrete is of important durability consideration.

Durability of concrete in sulfate water environment is mainly affected by its permeability. It is the major factor for deciding the long period durability of concrete in sulfate environment.

The sulfate resistance in concrete can be provided by using Portland cements that are low in their C_3A content. However, if sulfate resistant Portland cements are not readily available, OPC along with certain pozzolanas can also be used. But, the sulfate resistance of the mortar mix highly depends on the chemistry of the pozzolan used and its replacement level with cement (Venkatanarayanan et al. (2014)). Particularly, the ability of the pozzolan to reduce the permeability of the concrete cast is very important in reducing the sulfate attack.

In the present era, the utilization of Rice Husk Ash and Waste Paper Ash are the most active research areas that can cover a large number of concrete construction problems. The advantages of incorporating these supplementary cementitious materials despite of energy consumption saving (in cement production), lowering the cost of construction, and conservation of environment through reduction of waste deposit, can also improve the engineering properties of the concrete mix in terms of strength and durability considerations. Thus, the RHA, and WPA based geopolymer cements presents an interesting potential. Geopolymer concrete is also called as alkali activated concrete, because this concrete is formed by the alkaline activation of aluminosilicate material (Joshy M.B., Paul M.M. (2014)). RHA and WPA are having a good proportion of alumina and silica, which as mentioned are the good sources in creating the geopolymers.

This paper featured the study conducted on the use of the RHA and WPA based geopolymer concrete in ascertaining the behavior of the concrete during the normal and the sulfate water environment. The workability, compressive strength, split tensile strength, flexural strength, permeability, and the weight loss properties of the concrete adopted M20 Grade with the RHA, and WPA by the replacement of cement in the range of 5%, 10%, and 15%; and with the Mix (RHA+WPA) in the range of 5%, and 10% are stated.

2. RESEARCH METHODOLOGY

In the present research, cement has been partially replaced by RHA, WPA, and Mix (RHA+WPA) for M20 Grade of concrete. The replacement has been made in the range of 5%, 10%, and 15% of RHA and WPA, and for Mix (RHA+WPA) in the range of 5% and 10% by the weight of the cement. The research has been done for the properties like workability, compressive strength, split tensile strength, flexural strength, permeability, and weight loss both for the normal and the sulfate water environment. The specimens of standard cubes (150mmx150mmx150mm), standard cylinders (150mmϕx300mm height), and standard beams (100mmx100mmx500mm) were casted having different replacement levels of RHA, WPA, and Mix (RHA+WPA). The specimens were cured in the normal and the sulfate water for the required time. Equal number of specimens of cubes, beams, and cylinders were casted for the sulfate resistance. Sodium sulfate (Na_2SO_4) in the powder form was used to form 5% solution for creating the sulfate water environment

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3. MATERIALS USED AND THEIR PROPERTIES

In the present study, the materials used are Cement, Fine aggregate, Coarse aggregate, Rice Husk Ash, Waste Paper Ash, and Sodium Sulfate.

3.1 CEMENT

Ordinary Portland cement of Grade 43 from Ultra Tech Cement confirming to IS 8112-1989 has been used in this study. The physical analysis of cement was done using the respective IS codes and the properties are shown in the tabular form as:

Table 1. Properties of Cement

Property of cement	Results	IS -Code
Specific gravity	3.14	IS: 4031-PART 5-1988
Initial setting time	45 minutes	
Final setting time	350 minutes	
Consistency	35%	IS: 4031-PART 11-1988

3.2 FINE AGGREGATE

Natural river sand free from impurities with maximum nominal size of 4.75mm was used in this study. The physical properties confirming to respective IS codes are shown in the tabular form as:

Table: 2 Properties of fine aggregate

Property of fine aggregate	Results	IS –Code
Specific gravity	2.7	IS: 2386-1963
Moisture content	2.5%	
Zone	III	IS: 383-1970
Fineness modulus	3.4	

3.3 COARSE AGGREGATE

In the present study, 20mm of the maximum nominal size of coarse aggregate is used.

Physical properties confirming to IS: 2386-1963 are shown in the table below:

Table: 3 Properties of Coarse aggregate

Property of Coarse aggregate	Results	IS –Code
Specific gravity	2.63	IS: 2386-1963
Moisture content	1.976%	
Water Absorption	1.11%	

3.4 RICE HUSK ASH

In this study, RHA was purchased from the Jal Shri Balaji Refractories, Rajasthan, India. Table.4 shows the properties of the RHA as specified by the supplier, and also some were determined in the lab.

Table: 4 Physical properties of RHA

Property of RHA	**Results**
Appearance	Fine Powder
Silicon-dioxide Content	83.16%
Specific Gravity	2.45
Particle Size	Less than 45µ
Colour	Grey

3.5 WASTE PAPER ASH

Waste paper was taken from the Sharda University, Greater Noida, UP, India and was burnt in an open atmosphere. The ash was collected and sieved through the 90 micron IS sieve, after that it was further powdered into finer particles manually, and was then used for casting.

Some of the physical properties of WPA were found and are shown below:

Table: 5 Physical properties of WPA

Property of RHA	Results
Appearance	Fine Powder
Silicon-dioxide Content	Undefined
Specific Gravity	2.71
Particle Size	Sieved through 90μ IS sieve
Colour	Dark grey

3.6 SODIUM SULFATE

In the present study, the sulfate water environment was prepared by adding definite percentage of sodium sulfate (5%) in deionized water. The sodium sulfate was purchased from the Central Drug House (P) Ltd. Vardhan House, New Delhi.

Specifications as provided by the supplier:

Table: 6-Properties of Sodium Sulfate

Property	Results
Chemical Formula	Na_2SO_4
Physical state Colour Odor Ph of 5% solution	Powder White Odorless 5.2-9.2

4. MIX DESIGN

The concrete mix design was done by using IS 10262-2007 for M-20 grade of concrete. The calculated proportion for 1m^3 is given below:

Table: 7 Mix proportion for 1m^3

Material	Quantity
Grade	M20
Cement	383.22 kg/m^3
Fine aggregate	567.102 kg/m^3
Coarse aggregate	1224.9 kg/m^3
Water	191.61 kg/m^3
W/C ratio	0.5

The mix design ratio adopted was 1:1.479:3.19.

5. RESULTS

5.1 Tests on Fresh Concrete

a) Slump Test:

The slump value changes as the cement was replaced with the different percentage of the RHA, WPA, and Mix (RHA+WPA) in the concrete mixes. It can be understandably seen as the percentage of the RHA, WPA, and Mix (RHA+WPA) was increased, the slump value decreases.

The slump values are represented in the table below:

Table 8: Slump Test Result

Mix (M20)	Percentage	Slump value(mm)
Control Concrete	0%	72
RHA concrete	5%	69
	10%	58
	15%	32
WPA concrete	5%	64
	10%	56
	15%	34
(RHA+WPA) concrete	2.5%+2.5%	53
	5%+5%	30

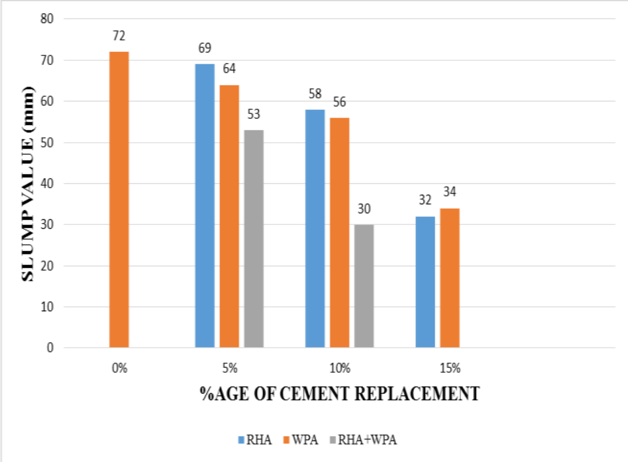

Fig. 1 Variation of Slump Value with RHA, WPA, and Mix (RHA+WPA)

5.3 Tests on hardened concrete

a) Compressive Strength Test:

CTM was used for the determination of the compressive strength of the cubical specimens at 7 and 28 days respectively. The load was applied gradually at the rate of 10 KN/sec.

a.1) For Normal Water Environment:

There is a consequential enhancement in the compressive strength with the RHA, WPA, and Mix (RHA+WPA). It can be clearly understood from data below that the compressive strength has increased up to 10% replacement level using WPA and also, the compressive strength attained at 10% replacement level with RHA, and Mix (RHA+WPA) is comparatively equal to the compressive strength of control concrete (variation is less than 5%). Beyond this replacement level, the compressive strength decreases. However, the maximum compressive strength at 28 days was attained for the replacement level of 5% WPA with value of 25.21 N/mm^2. The value of compressive strength with different levels of mix is shown below:

Table: 9 Compressive strength for Normal Water Environment

Mix (M20)	Percentage	Compressive strength (N/mm^2)	
		7 days	28 days
Control	0%	18.39	24.93
RHA	5%	19.41	24.95
	10%	18.11	24.42
	15%	16.50	23.16
WPA	5%	20.08	25.21
	10%	19.28	25.11
	15%	17.93	23.98
(RHA+WPA)	2.5%+2.5%	18.63	24.97
	5%+5%	17.97	24.81

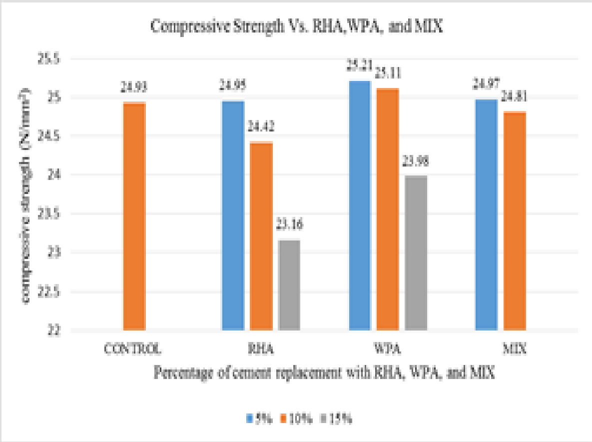

Fig. 2- Variation of 28-days Compressive Strength with RHA (%), WPA (%), and MIX (%)

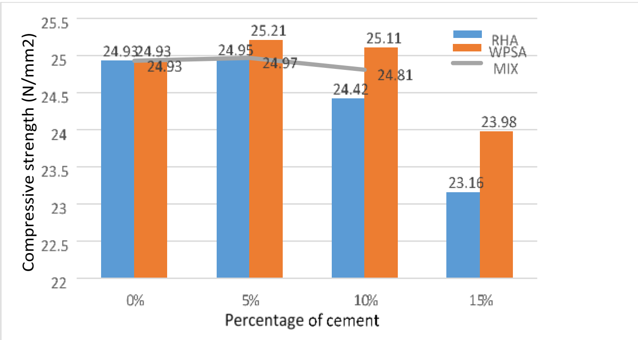

Fig. 3- Comparison of Compressive Strength between Control, RHA, WPA, and MIX (RHA+WPA) Concrete at 28 days

a.2) For Sulfate Water Environment:

The compressive strength increased with the increase in the percentage of RHA, WPA up to 15% replacement level and with Mix (RHA+WPA) up to 10% replacement level, which is patent that the RHA and WPA Concrete is having more sulfate resistance as compared to that of the OPC Concrete. The results obtained are shown in the table below:

Table: 10 Compressive strength for Sulfate Water Environment

Mix (M20)	Percentage	Compressive strength (N/mm²)	
		7 days	28 days
Control	0%	11.19	21.94
RHA	5%	13.59	21.97
	10%	15.45	22.06
	15%	16.02	22.15
WPA	5%	15.23	22.21
	10%	16.30	22.48
	15%	16.87	22.82
(RHA+WPA)	2.5%+2.5%	13.47	22.10
	5%+5%	15.62	22.36

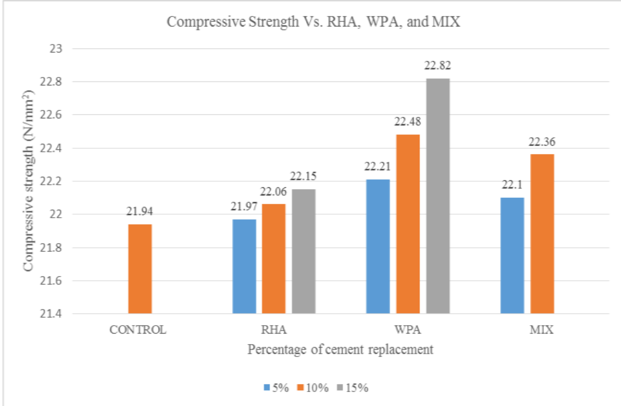

Fig. 4- Variation of 28-days Compressive Strength with RHA (%), WPA (%), and MIX (%)

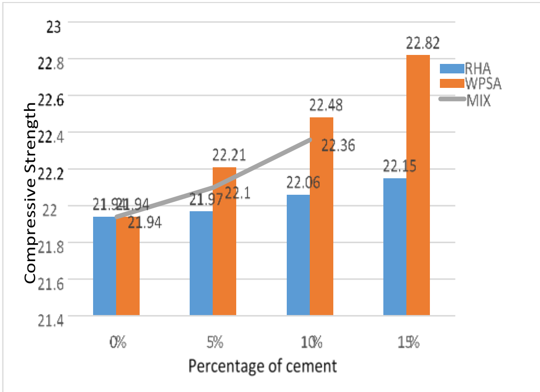

Fig. 5- Comparison of Compressive Strength between Control, RHA, WPA, and MIX (RHA+WPA) Concrete at 28 days

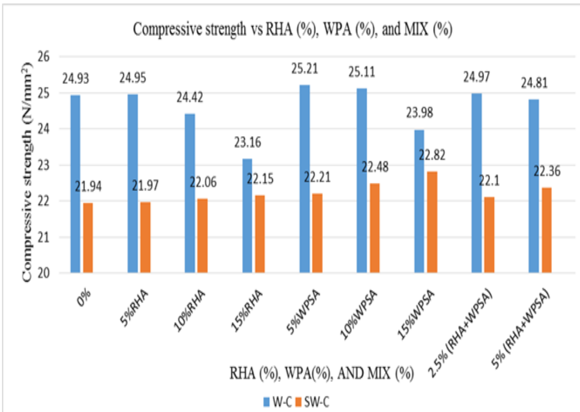

Fig. 6- Comparison of 28 days compressive strength during normal and sulfate water curing

WC-NORMAL WATER CURED
SW-C-SULFATE WATER CURED

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Table: 11. Loss (%) in Compressive strength

Mix (M20)	Percentage	Loss (%) in Compressive Strength at 28 days
Control	0%	11.99
RHA	5%	11.94
	10%	10.52
	15%	4.36
WPA	5%	11.90
	10%	10.47
	15%	4.83
(RHA+WPA)	2.5%+2.5%	11.49
	5%+5%	9.87

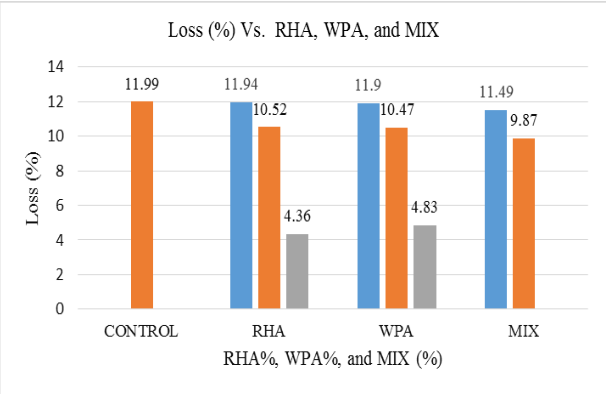

Fig. 7- Loss (%) in compressive strength at 28 days

b) Flexural Strength Test

b.1) For Normal Water Environment:

FTM with Ram dia. 81mm was used to determine the flexural strength of beam specimens at 7, and 28 days respectively. The load was applied at the rate of 180 kg/min slowly without any shock.

There is a considerable increase in the flexural strength with the increase in RHA, WPA, and MIX. It is clearly understood from the data obtained that the flexural strength has increased up to 10% replacement level using RHA, and MIX, and up to 15% replacement level using WPA. Beyond the 10% replacement level in case of RHA Concrete and MIX Concrete, the flexural strength shows a gradual decrease. However, the flexural strength attained at 5%WPA Concrete is maximum with the value of 5.11 N/mm^2. The value of Flexural Strength with different replacement levels of mix is shown below:

Table: 11. Flexural strength for Normal Water Environment

Mix (M20)	Percentage	Flexural Strength (N/mm^2)	
		7 days	28 days
Control	0%	3.61	4.93
RHA	5%	3.79	5.01
	10%	3.64	4.95
	15%	3.57	4.91
WPA	5%	3.82	5.11
	10%	3.75	5.03
	15%	3.64	4.97
(RHA+WPA)	2.5%+2.5%	3.81	5.09
	5%+5%	3.68	4.99

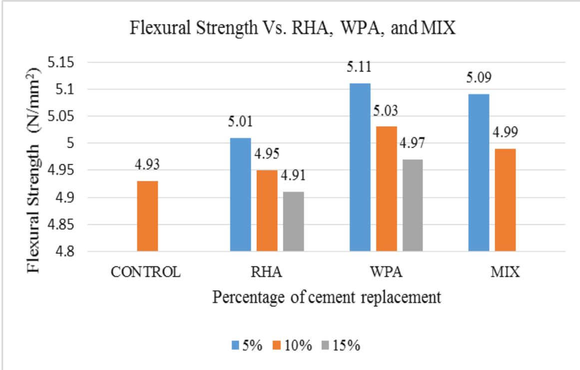

Fig. 8- Variation of 28-days Flexural Strength with RHA (%), WPA (%), and MIX (%)

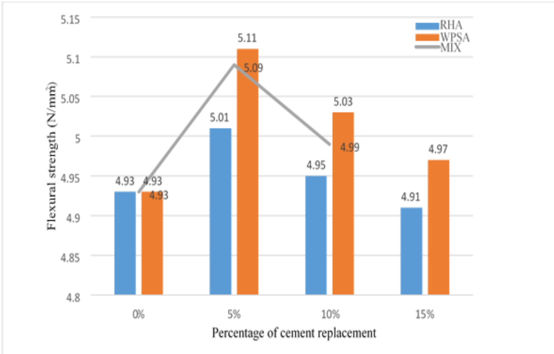

Fig. 9- Comparison of Flexural Strength between Control, RHA, WPA, and MIX (RHA+WPA) Concrete at 28 days

b.2) For Sulfate Water Environment:

The Flexural Strength increased as the percentage of RHA, WPA, and MIX was increased during the sulfate water curing up to the highest percentage adopted, that is up to 15% using RHA, and WPA, and up to 10% using Mix (RHA+WPA). The maximum value was obtained at the replacement with 15%WPA with the value of 4.25 N/mm^2. The results obtained are shown below:

Table: 12. Flexural strength for Sulfate Water Environment

Mix (M20)	Percentage	Flexural Strength (N/mm^2)	
		7 days	28 days
Control	0%	2.37	3.97
RHA	5%	2.42	4.13
	10%	2.51	4.15
	15%	2.57	4.20
WPA	5%	2.45	4.17
	10%	2.52	4.19
	15%	2.59	4.25
(RHA+WPA)	2.5%+2.5%	2.42	4.15
	5%+5%	2.56	4.18

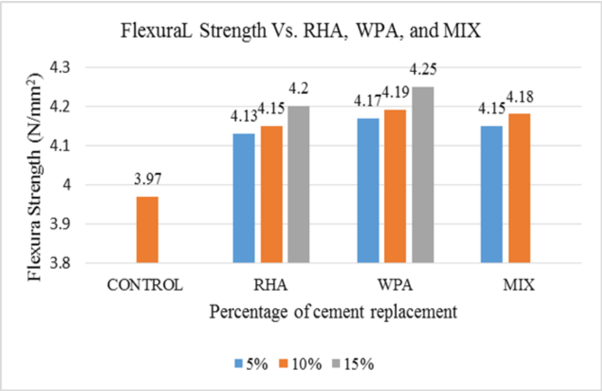

Fig. 10- Variation of 28-days Flexural Strength with RHA (%), WPA (%), and MIX (%)

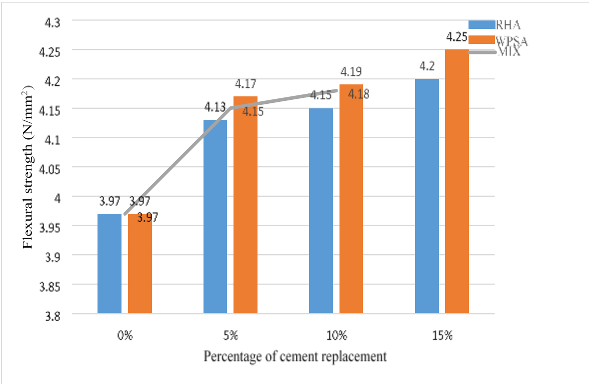

Fig. 11- Comparison of Flexural Strength between Control, RHA, WPA, and MIX (RHA+WPA) Concrete at 28 days

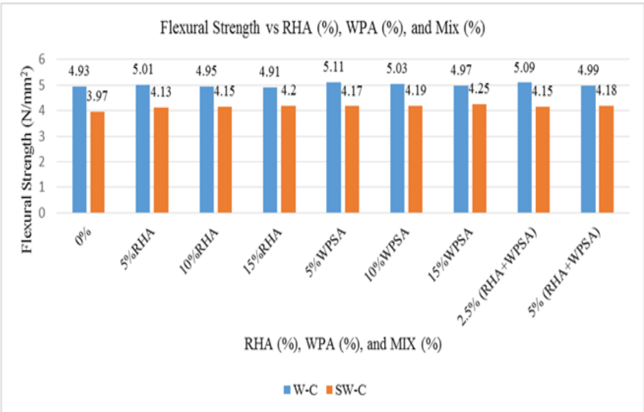

Fig. 12- Comparison of 28 days flexural strength during normal and sulfate water curing

Table: 13. Loss (%) in Flexural strength

Mix (M20)	Percentage	Loss (%) in Flexural Strength at 28 days
Control	0%	19.47
RHA	5%	17.56
	10%	16.16
	15%	14.28
WPA	5%	18.39
	10%	16.69
	15%	14.48
(RHA+WPA)	2.5%+2.5%	18.46
	5%+5%	16.56

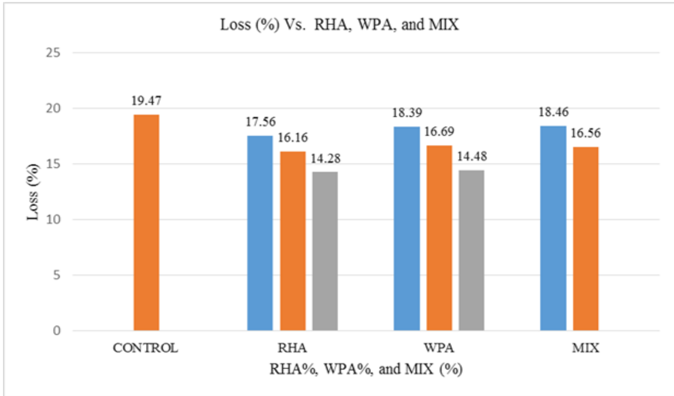

Fig. 13- Loss (%) in flexural strength at 28 days

b) Split Tensile Strength Test

b.1) For Normal Water Environment:

CTM (with Ram dia. 234) was used to determine the split tensile strength of cylindrical specimens at 7, and 28 days respectively.

There is a considerable enhancement in the split tensile strength because of RHA, WPA, and Mix (RHA+WPA). It can be clearly understood from the data below that the split tensile strength has increased up to 10% replacement level of RHA, WPA, and MIX with OPC. Beyond 10%, there is a considerable decrease in the split tensile strength of concrete mixes. However, the split tensile strength at 28 days is maximum for the 5% WPA concrete with the value of 2.59 N/mm^2. The value of split tensile strength with different levels of mix is shown below:

Table: 14. Split tensile strength for Normal Water Environment

Mix (M20)	Percentage	Split Tensile Strength (N/mm^2)	
		7 days	28 days
Control	0%	1.82	2.51
RHA	5%	1.92	2.55
	10%	1.84	2.52
	15%	1.71	2.37
WPA	5%	1.96	2.59
	10%	1.89	2.54
	15%	1.77	2.39
(RHA+WPA)	2.5%+2.5%	1.91	2.57
	5%+5%	1.85	2.53

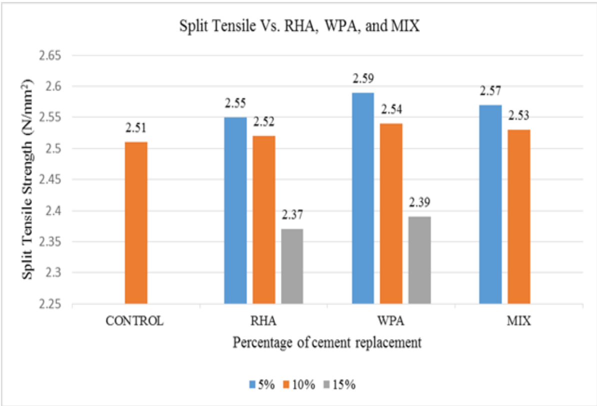

Fig. 14- Variation of 28-days Split Tensile Strength with RHA (%), WPA (%), and MIX (%)

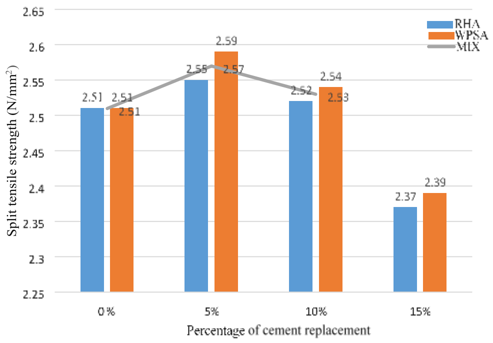

Fig. 15- Comparison of Split Tensile Strength between Control, RHA, WPA, and MIX (RHA+WPA) Concrete at 28 days

c.2) For Sulfate Water Environment:

The Split tensile strength increased as the percentage of RHA, WPA, and the MIX was increased during the sulfate water curing up to the highest percentage adopted. The maximum value was obtained for the replacement of cement with 15% WPA with the value of 2.37 N/mm^2 at 28 days. The results obtained are shown in the table below:

Table: 15. Split tensile strength for Sulfate Water Environment

Mix (M20)	Percentage	Split Tensile Strength (N/mm^2)	
		7 days	28 days
Control	0%	1.72	2.24
RHA	5%	1.75	2.29
	10%	1.79	2.31
	15%	1.83	2.35
WPA	5%	1.78	2.32
	10%	1.81	2.34
	15%	1.86	2.37
(RHA+WPA)	2.5%+2.5%	1.73	2.31
	5%+5%	1.79	2.33

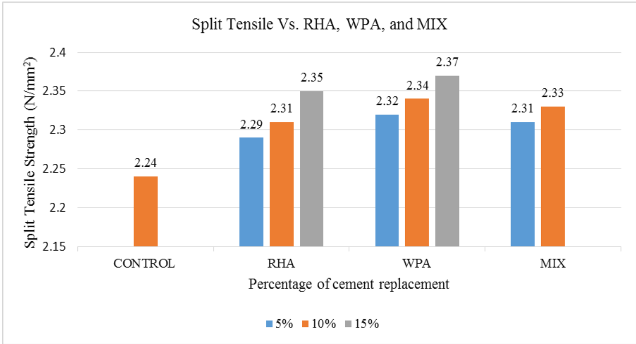

Fig. 16- Variation of 28-days Split Tensile Strength with RHA (%), WPA (%), and MIX (%)

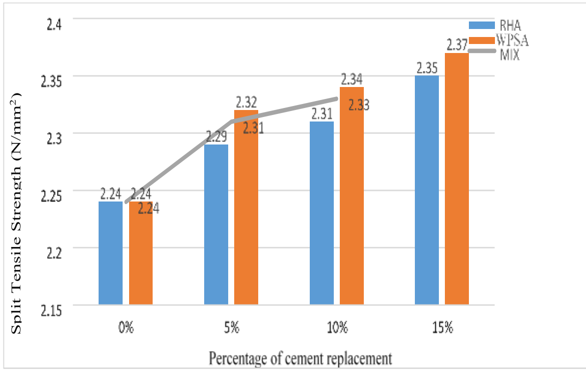

Fig. 17- Comparison of Split Tensile Strength between Control, RHA, WPA, and MIX (RHA+WPA) Concrete at 28 days

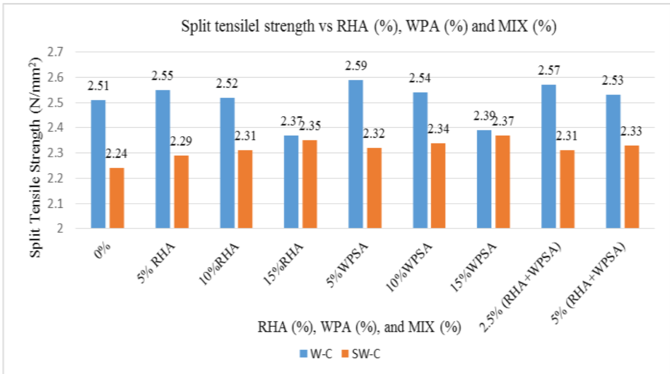

Fig. 18- Comparison of 28 days Split tensile strength during normal and sulfate water curing

Table: 16. Loss (%) in Split tensile strength

Mix (M20)	Percentage	Loss (%) in Split Tensile Strength at 28 days
Control	0%	10.75
RHA	5%	10.19
	10%	8.33
	15%	0.84
WPA	5%	10.42
	10%	7.87
	15%	0.83
(RHA+WPA)	2.5%+2.5%	10.11
	5%+5%	7.90

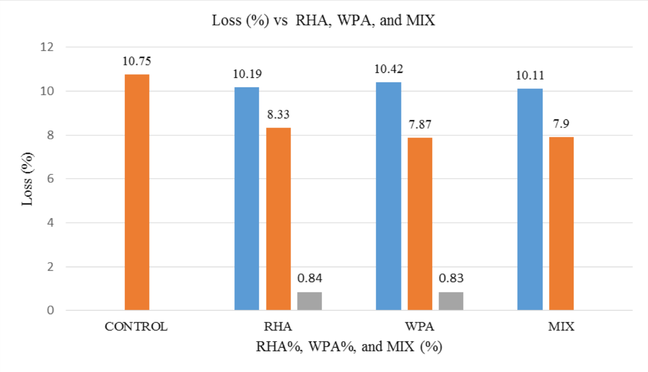

Fig. 19- Loss (%) in split tensile strength at 28 days

d) Water Permeability Test

To evaluate the depth of water penetration, the equal number of cube specimens of 10% RHA concrete, 10% WPA concrete, and control concrete were casted for both the normal water curing and sulfate water curing. The cubes were tested for permeability results at 28 days by using the Permeability testing machine. It is evident from the results that the RHA Concrete, and WPA concrete are less porous than the OPC control concrete. It is also understandable that the OPC concrete was about 2 times more permeable than that that of the 10%RHA concrete, and 10%WPA concrete. The RHA and WPA being pozzolanic materials occupied the hollow spaces in the concrete specimens and thus, resulted in the reduction of permeability of concrete. The results are shown in the table below:

Table: 17. Permeability Results for NW-C

Content	Mean Penetration at 28 days
Control Concrete	15mm
10% RHA Concrete	11mm
10% WPA Concrete	9mm

Table: 18. Permeability Results for SW-C

Content	Mean Penetration at 28 days
Control Concrete	20mm
10% RHA Concrete	14mm
10% WPA Concrete	12mm

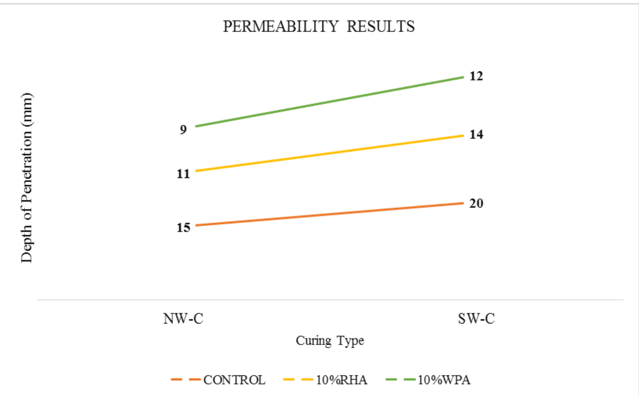

Fig. 20- Permeability Test Results at 28 days for NW-C and SW-C

e) Weight Effect

To observe the effect on the weight, the same number of specimens as casted for the permeability test were used, that is cube specimens of 10% RHA Concrete, 10% WPA Concrete, and Control concrete were examined at the 28 days of curing. It was observed that there was not much effect on the weight of the specimens during the Normal Water Curing. However, there was a considerable weight loss when the cubes were cured in the Sulfate Water, this is patent from the results shown below:

Table: 19. Weight loss (%)

Content	Weight (W1) after 28 days of NW-C (kg)	Weight (W2) after 28 days of SW-C (kg)	Weight Loss (%)
Control Concrete	8.005	7.857	1.848
10% RHA Concrete	8.101	7.985	1.431
10% WPA Concrete	8.109	8.001	1.234

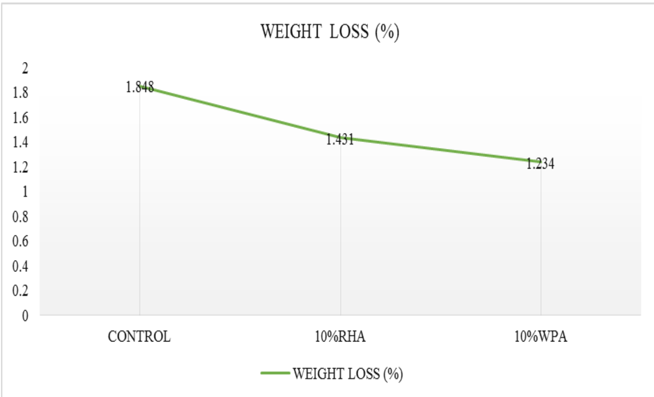

Fig. 21- Weight Loss (%) Results at 28 days of curing

6. CONCLUSION

1. Workability of the Geopolymer concrete mixes decreases with the increase in the percentage of geopolymer cement that is when cement was replaced with RHA, WPA, and MIX the water demand increases.
2. Geopolymer concrete shows an effective influence on the compressive, split tensile, and flexural strength.
3. Experimental study showed that it is possible to design M20 grade of concrete incorporating with RHA and WPA up to 10% replacement with cement, and the Mix (RHA+WPA) can also be adopted
4. Geopolymer concrete shows more sulfate resistance than the Control concrete. The sulfate resistance of mortars improved with increasing replacement levels of RHA, WPA, and MIX from 0 to 15%.
5. The performance of RHA and WPA at any given replacement levels was comparable, with the later performing slightly better.
6. The strength loss was more in Control concrete than in Geopolymer concrete. Loss in strength was lowered as the

percentage of RHA, WPA, and MIX was increased in the concrete.

7. The Geopolymer concrete was found to be 2 times less permeable than the Control concrete. The WPA concrete was found to be least permeable.
8. The weight loss was more in Control concrete than in the Geopolymer concrete.
9. Use of RHA, and WPA in concrete proved to be more economical & environmental friendly.

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