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A Study on Sulphuric Acid Attack on Concrete with Rice Husk Ash as a Partial Replacement of Cement

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Abstract:- Cement is widely noted to be most expensive constituents of concrete. Concrete is one of the most widely used construction materials, because of its good durability to cost ratio. Rice husk ash (RHA) is a highly reactive pozzolanic material suitable for use in mix for Portland cement as replacement. The possibility of using RHA as a construction material need to be investigates. The study suggests that up to 10% replacement of OPC with RHA has the potential to be used as partial cement replacement, having good compressive strength. Effect of sulphuric acid (H_2SO_4) present in mixing water on properties of setting times and compressive strength of cement concrete. The rate of development of compressive strength decreased with the increase in concentration of H_2SO_4 at 7days, 28days and 60 days

Keywords:- Rice husk ash ,Sulphuric acid, cement concrete, compressive strength, curing.

I. INTRODUCTION

Concrete is one of the most widely used construction materials, because of its good durability to cost ratio. The entire construction industry is in search of a suitable and effective the waste product that would considerably minimize the use of cements and ultimately reduces the construction cost. However, when subjected to severe environments its durability can significantly decline due to degradation of concrete. Cement using in concrete is a mixture of complex compounds. . The entire construction industry is in search of a suitable and effective the waste product that would considerably minimize the use of cements and ultimately reduces the construction cost.

Rice Husk is an agricultural waste obtained from milling of rice. About 108 tones of rice husk is generated annually in the world. Rice husk constitute about 1/5th of the 300 million metric tons of rice produced annually in the world. According to the report by Mehta (1992), the current yearly production paddy rice is approximately 500 million tones that gives about 100 million tones of rice husk as a waste product from the milling.

The reaction of these with water leads to setting and hardening of cement when it is gauged with water. Cement is a material with cohesive and adhesive properties when mixed with water, which makes it capable of bonding material fragments into a compact whole (Neville, 1996).Rice husk ash is one of the promising pozzolanic materials that can be blended with Portland cement for the production of durable concrete and at the same time it is a value added product. Addition of rice husk ash to Portland cement does not only improve the early strength of concrete, but also forms a calcium silicate hydrate gel around the cement particles which is highly dense and less porous, and may increase the strength of concrete against cracking (Saraswathy and Ha-Won, 2007).Chaudhary et al.,2001,has conducted various tests like Carbonation & pH test, Ultrasonic Pulse velocity test, Compressive strength test ofter 28 days plain concrete cubes ,it was observed that aggregates of plain concrete cubes in H_2SO_4,HCl & $(NH_4)2SO_4$ solutions were visible. It was due to washing out of cement paste. But in NaOH solution aggregate of concrete cube was not visible because cement paste was not washed out due to alkaline environment. On concrete which exposed to H_2SO_4 medium, Loss of cementitious property of concrete in H_2SO_4 medium was maximum and it was minimum in NaOH medium and also the loss in strength was due to expansive salt formation and weakening of bonds. Pande, and Makarande (2013,) has prepared cubes of 15 × 15 cm were tested, with 12.5, 25, & 37.5% of RHA, replacing in mass the cement and tested the properties like compressive strength, splitting tensile strength, water absorption and modulus of elasticity were evaluated. The results were compared to controlled sample and the viability of adding RHA to concrete. Replacement of 12.5 % of cement with rice husk ash in matrix causes reduction in utilization of cement and expenditures, improve quality of concrete at the age of 90 days and also addition of pozzolans like rice husk ash to the concrete, can improve the mechanical properties of specimens. Arunakanthi and Sudarsana Rao, (2013), study the metakaolin in which Ordinary Portland cement is partially replaced by 20% by weight and by subjecting the concrete curing to different concentrations of Sulphuric acid (H_2SO_4) in demonized water during mixing and curing.Based on the above results compressive strength and split tensile strength of HPC increased with the replacement of cement by 20% metakaolin. The strengths decreased with the increase in concentration of H_2SO_4 in mixing and curing water. Compressive strength and split tensile strength increase as the curing period decreases for later ages of curing i.e., 7 days, 28 days and 90 days for 20% metakaolin and for all concentrations of H_2SO_4. The results indicate that the compressive strength and split tensile strength decrease with the decrease in concentration of Sulphuric acid when compared with concrete without Sulphuric acid in mixing and curing water. Madhusudhana Reddy et al., (2012),"studied the effect of of sulphuric acid (H_2SO_4) on Blended Cement (fly ash based (BC)) and it's concrete. The BC and its concrete BCC produced with H_2SO_4 dosage of 100, 150, 300, 500 and 900 mg/l added in deionised water. In addition to this control specimens were prepared with deionised water (without H_2SO_4) for comparison. The results show that, as H_2SO_4 concentration increases, there is retardation in initial and final setting of cement (BC). The compressive strength of BCC has come down with an increase in the concentration of H_2SO_4 at both 28 and 90 days. Compressive strengths of BCC have decreased in the range of 2 to 23%, with an increase in H_2SO_4 concentration, when compared with the control specimens. Marthong (2012), has conducted a comparative study on effects of concrete properties when OPC 33, 43 and 53 of varying grades was partially replaced by RHA. Percentage replacement of OPC with RHA was 0, 10, 20, 30 and 40% respectively. The study suggests that up to 20% replacement of OPC with RHA has the potential to be used as partial cement replacement, having good compressive strength performance and durability. Test results indicate that RHA concrete can attain the same order of strength as conventional concrete at longer curing periods. However, the early strength development was observed to be about 50-60% of their 28 days strength. Nagrale et al., (2012), Sample Cubes were tested with different percentage of RHA and different w/c ratio, replacing in mass the cement. Properties like compressive strength, water absorption and slump retention were evaluated. With the addition of RHA weight density of concrete reduces by 72-75%.The cost of 1 m^3 of OPC concrete works out to Rs. 1157 while that of RHA concrete works out to Rs. 959. Thus, the use of RHA in concrete leads to around 8-12% saving in material cost. So, the addition of RHA in concrete helps in making an economical concrete. Akinkurolere (2013) carried out experimental studies to evaluate the influence of RHA on the Compressive strength of Recycled Aggregate Concrete cubes. The experimental variables used were the Water-cement ratio, Recycled Aggregate, and Rice-Husk Ash as partial replacement for cement. The results indicate that the strength development speed is faster for recycled concrete with a lower water-cement ratio. Karim et al., (2012) studied the influences of RHA on the strength of mortar and concrete and concluded that RHA could be used as supplementary cementing material up to a certain level of replacement (about 20-30% of binder) without sacrificing strength of concrete. Proper consumption of these RHA contributes in solving environmental pollution and production of cost-effective concrete; it can also play a vital role for the production of sustainable concrete. Abhilash Shukla et al., (2011), determine the optimum percentage (0, 5, 10, 15 & 20%) of RHA as a partial replacement of cement for M30 and M60 grade of concrete and also the effect of super plasticizer on mechanical properties. The increase in Compressive strength was of the order of 4.23% to 10.93% for M30 and M60 and at different ages i.e. 7 days and 28 days. There was also significant improvement in Flexural strength of the Concrete with rice husk ash content of 10% for different grades namely M30 and M60 and at the age of 28 days. Kartini et al., (2006), conducted study on the strength properties of rice husk ash concrete of M 30 with or without super plasticizer (Sp). The results reveal the influence of RHA on the workability of concrete and its strength performance by replacing OPC with different % of RHA. The water/binder ratio for these mixes were fixed at 0.63, 0.68 and 0.70 and designed to achieve slump in the range of 40 mm to 50 mm. The results of this study show that the combined effects of incorporating Sp and partial replacement of OPC with RHA provided higher compressive strength compared to the one without Sp, but the tensile strength without Sp at the later ages were better than OPC concrete. Sudarsana Rao et al., (2004), deals with the effect of hydrochloric acid (HCL) and sulfuric acid (H_2S0_4) mixing water and tested the properties of setting times, compressive strength and tensile strength of cement concrete and the results indicate that the initial and final setting times get retarded due to acidity imparted by HCL and H_2S0_4. The rate of development of compressive strength and tensile strength decreased with the increase in concentration of both HCL and H_2S0_4 for 28days and 90 days.

The main objective of this investigation is to evaluate rice husk ash as supplementary cementitious material with reference to mechanical properties of concrete and to identify the optimal level of replacement in concrete formation to reducing environmental problems associated with cement manufacturing and ash production. The effects of Sulphuric acid on setting, hardening and strength development of cement concrete are not known much. Hence, an investigation is carried out in order to evaluate the effect of sulfuric acid in setting time and strength of concrete under laboratory conditions. The results of the same are presented in this paper.

II. MATERIALS USED

A. Cement: Ordinary Portland (53 grade) Portland cement available in the local market of standard brand was used in the investigation. Portland cement is the most commonly used type of cement in the world today. It was tested as per Indian Standards Specifications IS: 8112-1989. Its properties are Specific surface area = 3200 cm^2/gm; Normal Consistency=31%; Initial and Final Setting Times are 50, 180 min., Specific Gravity=3.10; Fineness of cement by sieving through sieve No.9 (90 microns) for a period of 15 min. = 2.8%; Soundness = 1.29 mm and Compressive strength of cement (28 days) = 53 MPa respectively.

B. Rice Husk Ash: Rice Husk is an agricultural waste obtained from milling of rice. When rice husk is burnt in an uncontrolled manner, the ash, which is essentially silica, is converted to crystalline forms and is less reactive. The physical characteristics of the rice husk are Density=495Kg/m^3, Specific Gravity=2.53, Mean particle size=0.15-0.25 µm, Min specific surface area=220m^2/ kg, Particle shape= Spherical, and Moisture contents (% by weight) = 2.15and the chemical properties are SiO_2=75; Al_2O_3=1.29; Fe_2O_3 = 0.78CaO = 3.33; MgO = 0.22, MnO =0.20; Na_2O =0.40 ; K_2O =1.50; P_2O_5 = 0.59and Loss of ignition % by mass =3.67.

C. Fine Aggregate: The locally available natural river sand was used as fine aggregate. It was tested as per Indian Standard Specification IS: 383- 1970. Its fineness modulus is 2.74 and specific gravity is 2.6. The sand is free from clay, silt and organic impurities. These properties are Bulk Density (Kg/m^3) in loose state 1600 kg/m^3 and compacted density was 1750 kg/m^3. The fine aggregate conforms to standard specifications.

D. Course Aggregate: Aggregates are hard inert filler materials mixed with a binding material like cement lime or mud in the preparation of mortar or concrete. Machine crushed angular granite metal of 20 mm nominal size from the local source is used as coarse aggregate. The various properties of course aggregate are, specific gravity, bulk density and fineness modulus of coarse aggregate were found to be 2.62, 1580 kg/m^3 and 7.17 respectively.

E. Water: Water is a key ingredient in the manufacture of concrete. The locally available potable water accepted for local construction is used in the experimental investigation after testing. The pH value7, Suspended matter mg/lit=220, Organic matter mg/lit=20; Inorganic matter mg/lit=150; Sulphate (SO_4) mg/lit=30 and Chlorides (Cl) mg/lit=60.

F. Sulphuric Acid (H_2SO_4): Sulphuric acid is a very important commodity chemical, and indeed, a nation's sulphuric acid production is a good indicator of its industrial strength. Sulphuric acid reacts with its anhydride, SO_3, to form $H_2S_2O_7$, called pyrosulfuric acid, fuming sulphuric acid, Disulphuric acid or oleum or, less commonly, Nordhausen acid. Concentrations of oleum are either expressed in terms of % SO3 (called % oleum) or as % H_2SO_4 (the amount made if H_2O were added); common concentrations are 40% oleum (109% H_2SO_4) and 65% oleum (114.6% H_2SO_4). Pure $H_2S_2O_7$ is a solid with melting point 36 °C.

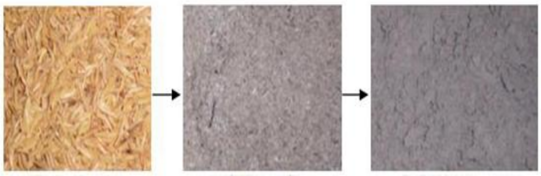

Fig .1 Production of RHA after Each Process

III. PREPARATION OF TESTING SPECIMEN

A. Mixing: Mixing of ingredients is done in pan mixer of capacity 40 liters. The cementitious materials are thoroughly blended and then the aggregate is added and mixed followed by gradual addition of water and mixing. Wet mixing is done until a mixture of uniform color and consistency are achieved which is then ready for casting. Before casting the specimens, workability of the mixes was found by compaction factor test.

B. Casting of Specimens: The cast iron moulds are cleaned of dust particles and applied with mineral oil on all sides before concrete is poured in to the moulds. The moulds are placed on a level platform. The well mixed green concrete is filled in to the moulds by vibration with needle vibrator. Excess concrete was removed with trowel and top surface is finished level and smooth as per IS 516-1969. The casting of test specimens is shown in Fig.: 2.

C. Curing of Specimens: The specimens are left in the moulds undisturbed at room temperature for about 24 hours after casting. The specimens are then removed from the moulds and immediately transferred to the curing pond containing clean and fresh water and cured for required period as per IS: 516-1969 as shown in Fig.3 & 4.

Fig. 2 Casted Specimens

Fig. 3 Specimens Cured in Water

Fig 4. Cured in Sulphuric acid (H_2SO_4) Solution

D. Description of Compression Testing Machine: The compression testing machine (Microprocessor based) used for testing the cube specimens is of standard make. The capacity of the testing machine is 2000 KN. The machine has a facility to control the rate of loading with a control valve .The plates are cleaned and oil level is checked, and kept ready in all respects for testing. After the required period of curing, the cube specimens are removed from the curing tank and cleaned to wipe off the surface water. It is placed on the machine such that the load is applied centrally. The smooth surfaces of the specimen are placed on the bearing surfaces. The top plate is bought in contact with the specimen by rotating the handle. The oil pressure valve is closed and the machine is switched on. A uniform rate of loading 140 kg/sq.cm/min is maintained.

Fig.5 Compression Testing Machine

IV. RESULTS AND DISCUSSIONS

The compressive strengths of concrete (with 0%, 5%, 10%, 15% and 20%, weight replacement of cement with RHA) cured in normal water for 7, 28, 60 days have reached the target mean strength .The compressive strengths of concrete (with 0%, 5%, 10%, 15% and 20%, weight replacement of cement with RHA) cured in water for 7, 28 and 60 days and the strengths (Table.1).

Table I: Variation of Compressive Strength of Concrete Cubes vs. Different % of RHA in H_2SO_4 Curing

Water				1% H_2SO_4			3% H_2SO_4			5% H_2SO_4		
Compressive Strength(Days)Mpa												
% of RHA	7	28	60	7	28	60	7	28	60	7	28	60
0	37.95	45.95	56.5	34.9	42.1	54.5	31.12	34.5	46	20.2	26	32
5	39.05	46.86	56.95	36.2	43.2	55	31.9	36.5	47.1	21.9	27	32.6
10	39.25	47.92	57.8	37.2	44.5	55.9	32.5	39	49.6	22.5	28.2	33.2
15	37.2	45.85	55.18	35.3	42.9	52.2	31.85	34	45.6	21.8	25.6	32.2
20	36.34	44.14	53.95	34.4	40.85	51.1	30.95	33.9	44.9	20.5	24	29.95

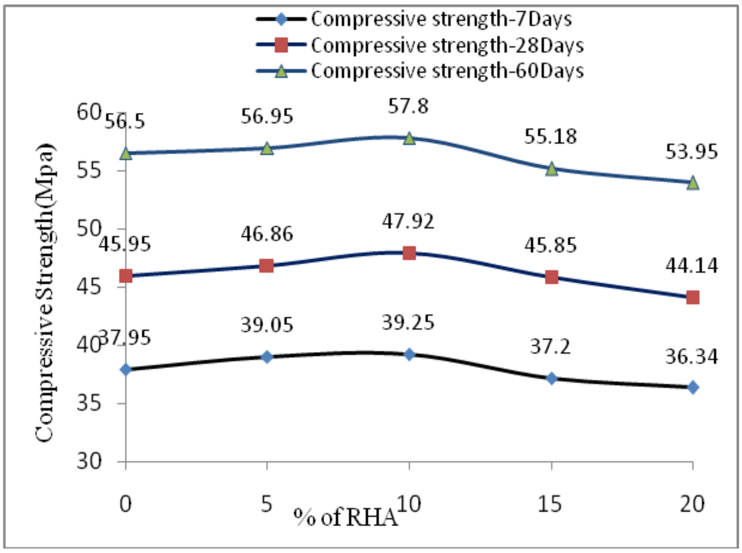

Fig.6 Compressive Strength of Concrete Cubes vs. Different % of RHA in Water Curing

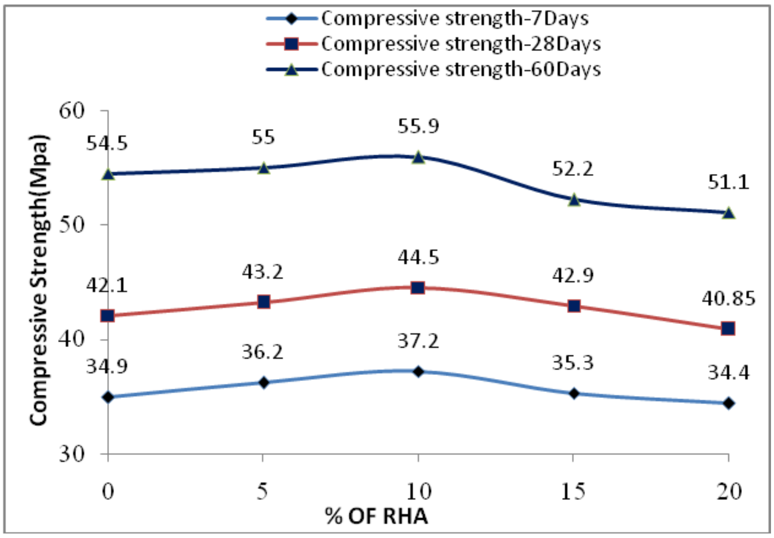

Fig.7 Compressive Strength of Concrete Cubes vs. Different % of RHA in 1% H_2SO_4 Curing

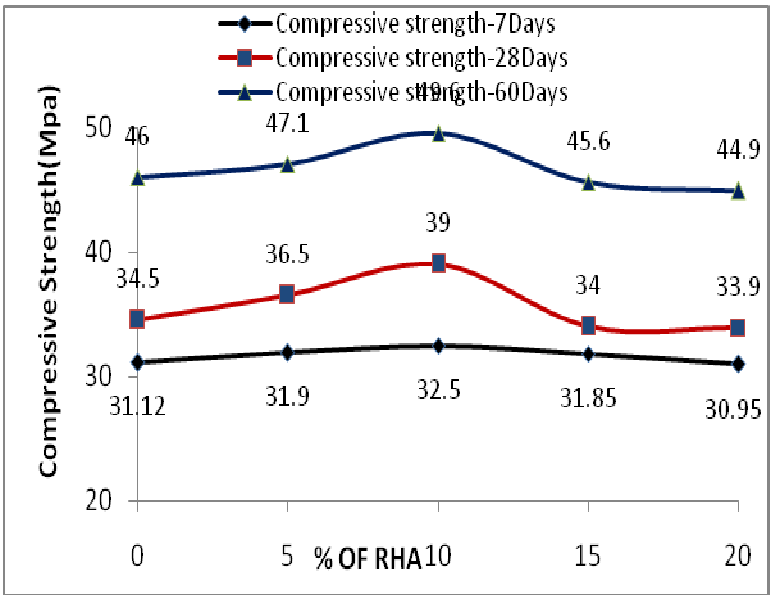

Fig.8 Compressive Strength of Concrete Cubes vs. Different % of RHA in 3% H_2SO_4 Curing

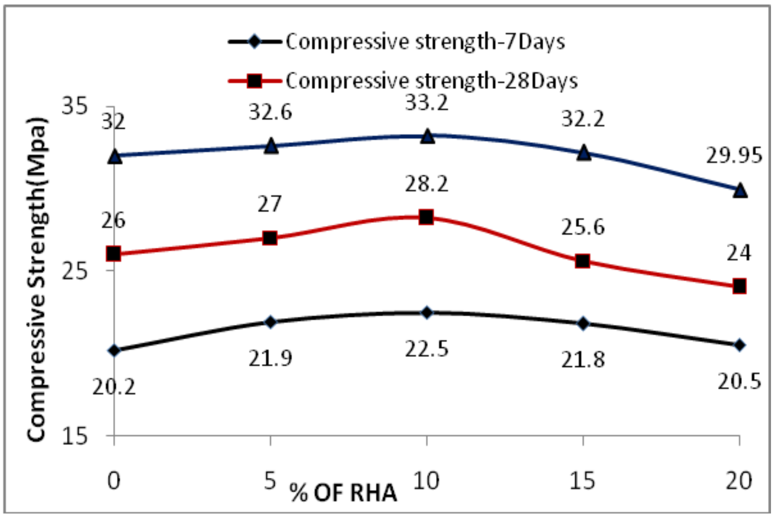

Fig.9 Compressive Strength of Concrete Cubes vs. Different % of RHA in 5% H_2SO_4 Curing

The test results indicate that at 5% replacement there is increase in strength, maximum strength obtained at 10% and starts reduced at 15% replacement but at 20% replacement of RHA decrease the strength. The compressive strengths of concrete (with 0%, 5%, 10%, 15% and 20%, weight replacement of cement with RHA) cured in Sulphuric acid solution for 7, 28 and 60 days at different percentages of sulphuric acid shown in Tables 1 and Figs 6 to 9, indicate that at 1% sulphuric acid curing decrease in strength of 5%, 20% strength at 3% sulphuric and 45 % strength reduction at 5% sulphuric acid curing indicates a measure of weight loss and leads to disintegration due to acid attack .This reduction in strength was mainly due to expansive salt formation. The formation of expansive salt also resulted in loss of cementitious properties. The concrete exposed to H_2SO_4 solution was found least durable.

Sulphuric Acid attack on Concrete: The loss of weight of concrete cubes in H_2SO_4 medium is due to ettringite formation. Sulphuric acid attacks on Ca (OH)s and form CaSO4 which is leached out of concrete easily. The calcium silicate hydrate reacts with H_2SO_4 to form fragile silica gel which is easily destroyed by external physical forces. The calcium sulphate formed by initial reaction can proceed to react with calcium aluminate phase in cement to form voluminous calcium sulpho aluminate (ettringite) which can cause expansion, cracking, loss of weight & strength and disintegration of concrete.
The chemical reaction involved in H_2SO_4 attack on cement concrete can be represented as follows.
$Ca(OH)_2 + H_2SO_4 = CaSO_4.2H_20$
$3\ CaO, Si0_2.3H_2 0 + H_2SO_4 = CaSO_4.\ 2H_20 + Si(OH)_4$
$3\ CaSO_4 + 3CaO.\ Al_20_3.6\ H_2O + 25\ H_2O = 3CaO.\ Al_20_3.3CaSO_4 + 31\ H_2O$

V. CONCLUSIONS

- The compressive strengths of concrete (with 0%, 5%, 10%, 15% and 20%, weight replacement of cement with RHA) cured in Normal water for 28 days have reached the target mean strength.
- The compressive strength of concrete with RHA concrete is less in Sulphuric acid environments compared to that of in normal concrete.
- The compressive strengths of concrete (with 0%, 5%,10%,15% and 20%, weight replacement of cement with RHA) cured in Sulphuric acid solution for 7, 28 and 60 days, indicate that up to 10% replacement there is increase in strength and beyond that the strengths decreased , but at 20% replacement RHA strength less than to normal concrete.
- The strength decreases in acidic environment with age of concrete also with increasing of RHA content in concrete.
- The compressive strengths of concrete (with 0%, 5%, 10%, 15% and 20%, weight replacement of cement with RHA) cured in Sulphuric acid solution for 7, 28 and 60 days indicates that continuous decrease in strength due to acid attack at the rate of 5%, 20% and 45% at 1%, 3% and 5% of Sulphuric acid solution curing indicates a measure of weight loss and leads to deterioration.
- In concretes cement can be replaced with 10% RHA with maximum increase in strength beyond starts decreases and due to slow pozzolanic reaction the Rice Husk Ash (RHA) concrete achieves significant improvement in its mechanical properties at later ages.

- There was severe deterioration of concrete exposed to H_2SO_4 and loss of cementitious property of concrete was observed.

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