



Resistance of Wood Ash Concrete to Sulfuric Acid Attack

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ABSTRACT

This paper presents the residual compressive strength of wood ash (WA) concrete cube specimens after immersion in diluted sulfuric acid (H_2SO_4) solutions. The sulfuric acid resistance of WA concrete is observed using 2% and 5% H_2SO_4 solutions. WA is used as mineral admixture and the partial substitution levels of WA are 0% (CW0), 5% (CW5), 10% (CW10), 15% (CW15), and 20% (CW20) by weight of 53 grade Portland cement. WA concrete results are compared with the results of M30 grade concrete (CW0). At CW5 and CW10 replacement levels, a slight enhancement in the strength of WA concrete is noticed. No significant resistance to H_2SO_4 is observed with WA concrete when compared with CW0 concrete. Further, the deterioration of CW0, CW5, and CW10 concrete is similar. The substitution of WA with cement reduces the cement content and eventually gives fewer hydrated cementitious products that enable deterioration by H_2SO_4 . Furthermore, WA helps in improving the density and filling capacity of the interaction transition zone of concrete which leads to the reduction of pores and capillary action. In brief, the use of WA in concrete benefits by converting environmental concern material into a sustainable resource in producing cementing materials.

Keywords: Wood ash, Sustainable concrete, Sulfuric acid, Acid attack, Residual strength.

INTRODUCTION

Concrete an extensively used construction material is alkaline with a pH value of 12–13.5, which makes it more susceptible to acid attacks¹. Structures maintenance and life cycle performance are affected by the degradation of hardened cement matrix and aggregates, caused by the acid attack. The severity of dissolution caused by an acid attack depends on the acid type and pH value². Considering the pH value, the deterioration of concrete is classified into

three zones namely degraded zone, transition zone, and intact zone. Acidic sources having a pH value of <4.5 deteriorates concrete severely. Nevertheless, the pH value alone cannot forecast the severity of deterioration^{3,4}. The complexity involved in acid corrosion cannot be identified by a single parameter and the degradation rate is defined by the loss of strength and mass and change in dimension of the specimen with time and is related to the chemical kinetics^{5,6}. The factors that influence the severity of the acid attack on concrete mainly depend on



the quality and type of cement, admixtures used, thickness and stability of the concrete surface, the diffusivity of acid, permeability nature of concrete, volume stability, and solubility of calcium salt of source acid, anion type and pH of the acidic solution^{7,8}. The various processes of deterioration of concrete or cementitious materials may be of mechanical, chemical, or physical sources, as an outcome of internal or external causes. Sewer systems, industrial environment, and acid rains are the main sources of acidic environments for concrete and cementitious materials. The availability of H_2SO_4 in surrounding environments may be by chemical origin, biogenic origin, and industrial discharges. The presence of H_2SO_4 in these environments when comes into contact with concrete elements, deterioration occurs. The generation of biogenic-based H_2SO_4 includes several biological and chemical processes⁹. It is well established that sulfate ions react with the hydrous products of cementitious paste to generate expansive products like thaumasite, gypsum, and ettringite, which results in spalling, cracking, and volume expansion and strength loss. Further, the deterioration of concrete significantly increases the hydraulic flow rate and diffusion rate and consecutively enhances the deterioration process. Sulfate sources when comes into contact with concrete, the damage proceeds from the surface into the core through the voids or capillary pores. The corrosion of concrete due to the sulfate attack is expressed as a function of the progress rate, the quantity of expansion, and the depth of attack. The sulfate attack negatively affects the properties of concrete like deformation capacity, stiffness, durability, and strength.

H_2SO_4 is considered the most offensive mineral acid present in the surrounding environment to concrete, which is mainly produced by (i) the oxidation of sulfur oxides generated by industrial activities and automobiles¹⁰. (ii) In sewer systems, sulfur compounds are decomposed by the action of bacteria that ultimately produces sulfuric acid^{10,11}. (iii) H_2SO_4 may also be produced by the oxidation of pyrite which is widely and abundantly available in the earth's sulfide minerals¹². Concrete when comes into contact with sulfuric acid form calcium sulfate. This calcium sulfate tends to produce expansive products and stimulate the sulfate attack in concrete. The deterioration of concrete elements exposed to H_2SO_4 results in both economic and environmental problems.

The factors influencing the concrete corrosion by sulfuric acid can be divided into two types: (i) external factors such as the stress state of concrete, temperature, and pH value of the solution. (ii) internal factors such as quality of aggregate, water to cement ratio, and chemical and mineral admixtures¹³.

In an anaerobic environment, sulfate-reducing bacteria absorb the sulfate content available in the sewer systems and release sulfide ions. These ions react with the available hydrogen dissolved in sewer systems and form hydrogen sulfide (H_2S). The H_2S when absorbed into concrete elements reacts with the available oxygen (O_2) and forms elemental sulfur (S). Furthermore, the sulfate oxidizing bacteria metabolize sulfur to form H_2SO_4 on the concrete surface. In the acidic environments, during the reaction process calcium aluminate and calcium hydroxide will get dissolved. Firstly, H_2SO_4 reacts with calcium hydroxide forming gypsum. The production of gypsum involves the generation of whitish and soft corroded surfaces which results in volume expansion of concrete creating deterioration. Further, calcium aluminate may react with the newly formed gypsum to ettringite⁹.

Wood ash (WA) is a waste fine powder obtained after the burning of waste wood particles such as bark, sawdust, and chips. In general, wastes from wood-related sources are used as combustion fuel in producing heat energy for industrial and household purposes. The physicochemical properties of WA primarily depend on the species of the wood, incineration temperature, supplementary fuels used, and the efficiency of the boiler. On average, the incineration of wood produces nearly 6% to 10% of ashes¹⁴⁻¹⁶. The viability of the use of WA in concrete is governed by its chemical compounds. The major compounds found in WA are magnesium (1%-2%), carbon (4%-34%), manganese (0.3%-1.3%), potassium (3%-4%), calcium (7%-34%), sodium (0.2%-0.5%), and phosphorus (0.3%-1.4%). Some traces of molybdenum, copper, zinc, and boron are also found at per million levels. Typically, WA also consists of SiO_2 , $CaCO_3$, and $K_2Ca(CO_3)_2$ which confirms the alkaline nature and will have a positive effect on the hydration process of cement¹⁶.

In this study, an effort is made to experimentally study the possibility of the use of WA as mineral admixture and partial

substitute to cement for producing sustainable and eco-friendly concrete. The sulfuric acid resistance of WA concrete is observed using 2% and 5% H₂SO₄ solutions. The experimentally obtained results are compared with the results of M30 grade concrete. For this aim, the locally available WA is employed in the present research.

MATERIALS AND METHODS

Table 1 shows the concrete mix proportions. Locally available Portland cement (OPC 53 grade) in agreement with IS 12269:2013¹⁷ with a specific gravity of 3.15 is used. The water used in mixing the concrete constituents is potable and is collected from the laboratory water grid which is free from organic materials and suspended solids. Crushed coarse aggregate with 20 mm of maximum size is used in accordance with IS 383: 2016¹⁸ with specific

gravity and fineness modulus of 2.86 and 6.82. Clean river sand is obtained from the local resources and collected from the Krishna river. WA is collected from a hotel central cooking system in Guntur city. M30 grade concrete is designed as per IS 10262: 2019¹⁹. Fig. 1 shows the locally available WA that is used for the experimental study.



Fig. 1. WA used for experimental study

Table 1: Concrete mix proportions

S.No	Mix ID	Wood ash (%)	Wood ash	Cement	Natural Sand	Crushed Coarse aggregate	Water (lts)
1	W0	0%	0.0	420.0	634.2	1184.4	168
2	W5	5%	21.0	399.0	634.2	1184.4	168
3	W10	10%	42.0	378.0	634.2	1184.4	168
4	W15	15%	63.0	357.0	634.2	1184.4	168
5	W20	20%	84.0	336.0	634.2	1184.4	168

*The constituents are in (kg/m³)

Concrete cube specimens (100 mm) are cured for 28 days in water, and then specimens are air-dried for 24 hours. H₂SO₄ solutions (2% and 5% concentrations per volume) are prepared by mixing dilute H₂SO₄ with water. Later three concrete cube specimens from each mix are immersed in 2% and 5% H₂SO₄ solution for a duration of 28 days, as seen in Fig. 2. After 28 days of exposure to 2% and 5% H₂SO₄ solution, the cubes are removed and the surfaces are cleaned with a dry cloth and kept undisturbed for 2 hours. H₂SO₄ resistance is evaluated by determining the compressive strength and mass loss²⁰.

RESULTS AND DISCUSSION

Figure 3 presents the three concrete cubes that are cast and tested for each average compressive strength value of CW0, CW10, CW15, and CW20 concrete. The compressive

strength of CW0, CW5, CW10, CW15, and CW20 at the age of 7 days is 26.3, 27.9, 25.2, 22.8 and 20.2 MPa, respectively. At 7 days, for CW5, CW10, CW15, and CW20 concrete, the compressive strengths are 106.08%, 95.82%, 86.69%, and 76.81% of CW0, respectively. At 28-days, the compressive strength results of CW0, CW5, CW10, CW15, and CW20 are 41.4, 43.5, 40.2, 37.3, and 34.5 MPa, respectively. At 28 days, for CW5, CW10, CW15, and CW20 concrete, the compressive strengths are 105.07%, 97.10%, 90.10%, and 83.33% of CW0, respectively. The highest compressive strength is observed for the CW5 mix. This could be due to the reactive nature of amorphous silica and alumina that are present in WA. For mix CW20, the strength is decreased by the addition of WA. This may be due to the dilution effect of WA in concrete and the lessening in the cement content.



Fig. 2. A view of the test setup of cubes immersed in sulfuric acid solutions

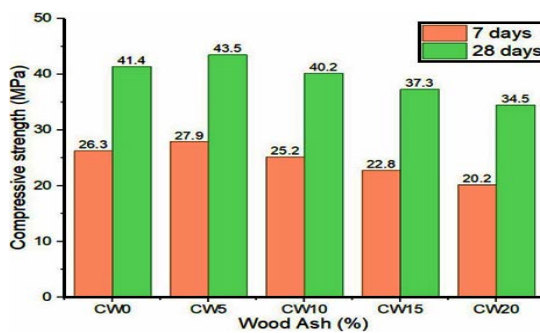


Fig. 3. Compressive strength of concrete at 7 and 28 days

Residual compressive strength and mass loss

Figure 4 presents the average residual compressive strength values of concrete specimens, after immersion in 2% and 5% H_2SO_4 solution. The residual compressive strength of CW0, CW5, CW10, CW15, and CW20 after immersion in 2% H_2SO_4 solution is 28.10, 28.90, 26.31, 23.67, and 21.31 MPa, respectively. After immersion in 2% H_2SO_4 , the residual compressive strength when compared with the 28-day compressive strength of CW0, CW5, CW10, CW15, and CW20 is reduced by 32.12%, 33.56%, 34.55%, 36.54%, and 38.22%, respectively. The residual compressive strength of CW0, CW5, CW10, CW15, and CW20 after immersion in 5% H_2SO_4 solution is 16.29, 16.34, 14.75, 12.88, and 10.58 MPa, respectively. After immersion in 5% H_2SO_4 , the residual compressive strength when compared with the 28-day compressive strength of CW0, CW5, CW10, CW15, and CW20 is reduced by 60.55%, 62.44%, 63.31%, 65.47%, and 69.33%, respectively. Fig. 5 shows a view of specimens after exposure to H_2SO_4 solution. Before testing the specimens for compressive strength, the specimens are removed from the

H_2SO_4 solution and then surfaces are cleaned. A washable or easily removable whitish layer can be seen on the surface of concrete specimens, which is formed as a result of immersion in H_2SO_4 solution. Fig. 6 shows a view of the deterioration of CW20 concrete specimens after exposure to H_2SO_4 . The mass loss (%) of concrete specimens after immersion in 2% and 5% H_2SO_4 solutions is shown in Fig. 7. The highest rate of mass loss is observed with CW20 and the lowest is observed with CW0 concrete specimens.

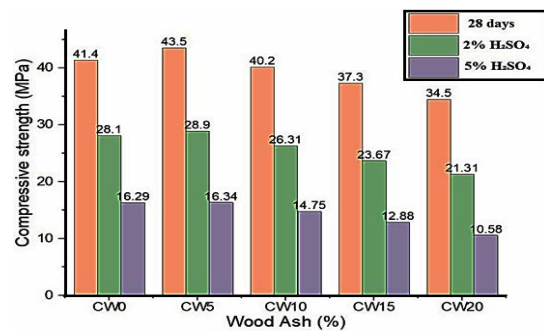


Fig. 4. Residual compressive strength of concrete cube specimens after the sulfuric acid attack



Fig. 5. A view of concrete cube specimens after being exposed to sulfuric acid

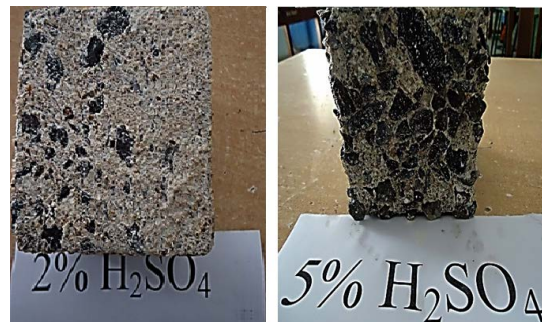


Fig. 6. A view of CW20 concrete specimens after exposure to sulfuric acid

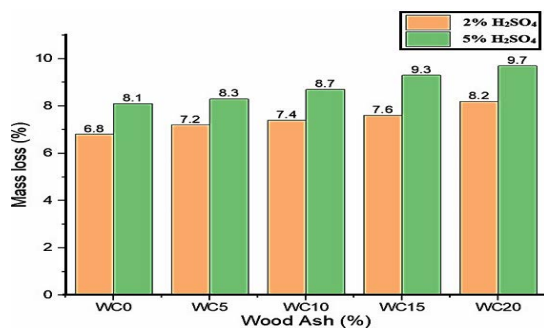


Fig. 7. Mass loss (%) of concrete after the sulfuric acid attack

The combination of pozzolanic materials with cement reduces the formation of portlandite and forms a new calcium silicate hydrate (CSH) which varies by ordinary CSH. CSH formed by the pozzolanic combination is more stable and durable in low pH surrounding environment. The acid resistance of concrete mainly depends on the concrete composition and cement type. ASTM C150 Type II and IV are examples of sulfate-resistant Portland cement made by reducing the C3A content. Another method for increasing concrete's acid resistance is incorporating mineral admixtures in concrete production. The mineral admixtures could be used as mineral addition, partial cement replacement, and binary or ternary blended cement^{20,21}. It is evident that concrete deterioration under acidic environment is a continuous process and acid penetrates into the specimen until they are immersed in the H₂SO₄ solution.

In this experimental investigation, all the specimens exhibited a loss in strength and mass when immersed in H₂SO₄. This loss can be attributed to the H₂SO₄ attack on CH and CSH phases present in concrete. Furthermore, H₂SO₄ introduces H⁺ and SO₄²⁻ into the pore water which helps in sulfate attack. H⁺ ions react directly with CSH and CH phases and SO₄²⁻ ions help in the formation of an expansive product ettringite. On the other hand, the micro-cracks formed on the surface of the concrete specimens by the H₂SO₄ attack act as pathways for the penetration of potential ions and deteriorate the core concrete.

The reduction in the properties of concrete cube specimens after immersion in 2% and 5% H₂SO₄ solutions could be attributed to the corrosion of concrete made by the H₂SO₄ in reaction with

calcium hydroxide forming gypsum. Further H₂SO₄ reacts with the free calcium aluminate hydrate (C-A-H) and generates calcium sulfoaluminate, which produces volume expansion of cementitious materials that has a destructive character like a reduction in mass, bonding, and strength. The decrease in the strength of concrete specimens is high with a 5% H₂SO₄ solution than with 2% H₂SO₄. This can be accredited to the high leaching phenomenon of cementitious material caused by the higher acid concentration. The severity of the deterioration of concrete mainly depends on the quality of the cement matrix/hardened paste and the available capillary pores on the surface. The substitution of WA in concrete up to 10% showed similar deterioration that with CW0 concrete. However, the adverse effect shown by CW15 and CW20 concrete specimens could be due to the high replacement levels of WA with cement that leads to the dilution effect of WA in concrete.

CONCLUSION

WA concrete is prepared from the locally available WA resources. This directly helps in decreasing the quantity of use of cement and indirectly helps in reducing the consumption of raw materials that are used for producing cement. WA properties may vary in quality and magnitude by their production processes like kind of wood and incineration technique.

From the experimental results, it is noticed that up to 10% WA can be used as mineral admixture and partial substitution for cement. Further substitution of WA resulted in a small decrease in the compressive strength. The pozzolanic reaction of WA concrete enhanced the durability of concrete which eventually reduces the disintegration tendency to H₂SO₄. The substitution of WA in concrete up to 10% showed similar deterioration that with CW0 concrete. However, the adverse effect shown by CW15 and CW20 concrete specimens could be due to the high replacement levels of WA with cement that leads to the dilution effect of WA in concrete. The substitution of WA with cement reduces the cement content and eventually gives fewer hydrated cementitious products that enable deterioration by H₂SO₄. Furthermore, WA helps in improving the density and filling capacity of the interaction

transition zone of concrete which leads to the reduction of pores and capillary action.

In brief, the use of WA in concrete benefits converting environmental concern material into a sustainable resource in producing cementing materials. In the future, this experimental study may be extended to study the properties of WA concrete under different environmental conditions.

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Conflict of Interest

The authors declare that we have no conflict of interest.

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