



Use of Biochar as a Pozzolanic Material and its Role in Mechanical Properties of Cement Concrete

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Abstract

Industrial waste materials such as fly ash, silica fume, blast furnace slag and lime stone powder etc have been blended successively with cement for their pozzolanic property. But, agricultural waste products like the straw of rice, wheat and other millets are left in the field and set in fire for clearing the field for next cultivation and affects the atmosphere severely. Though these materials have some pozzolanic quality, it is not generally used. Here, a study has been made to investigate the pozzolanic quality of rice straw and its use as an additive to cement. Biochar prepared by pyrolysis of rice straw enhances the setting time, increases the strength and reduces the permeability of cement concrete when mixed partially with cement.

Key words: Biochar, pyrolysis, workability, permeability, filler material

Introduction

Pozzolanic materials such as fly ash, silica fume etc. are added in ordinary Portland cement to produce pozzolana Portland cement. The pozzolanic additives act both as a cementitious admixture as well as a fine filler. Pozzolans contain predominantly silica and alumina and combine with Portland cement in the presence of water to produce new reaction products having binding character. It depends upon the amount of tricalcium silicate (C3S) and dicalcium silicate (C2S) in the cement. Each of these compounds react with water to form C-S-H (calcium silicate hydrate) and portlandite – Ca(OH)₂. Pozzolanic activity decreases the hydration heat by replacing a part of cement. Due to limited solubility of these hydration products, particles of hydrated lime form within interstitial spaces. With a continuous supply of moisture, the lime reacts with the silica of fly ash producing additional hydration products of a fine pore structure. The hydration products produced fill the interstitial pores reducing the permeability of the matrix.

Large scale burning of agricultural wastes like stalk of rice, wheat and other millets and its detrimental effect on environment has drawn the attention of researchers for a beneficial use of these waste materials. The global carbon dioxide emissions hit a record high of 33 billion tons in 2019 (Saint Akadiri et al. 2020) of which cement production was responsible for about 1.8×10^9 tons accounting for 5%–8% of the global anthropogenic emissions. A new carbon sequestration technology is to pyrolyze biomass to biochar and

then to use pulverized biochar as a cement supplementary material. This process reduces cement production and locks carbon in inert cementitious materials simultaneously (Carmi et al. 2019).

Different uses have been made from these products depending on their chemical composition. Biochar (BC) is such a waste product prepared from agricultural wastes like stalk of rice and wheat by process of pyrolysis. BC contains silica and calcium as other pozzolanic (Zubin 2010, Singh et al. 2010) materials and the morphology, texture and some surface properties of biochar makes it a potential pozzolanic material to be blended with cement. The critical factors such as preparation condition and properties of BC suitable for carbon sequestration has been studied by Gupta and Kua (2017). The additives in cement composite C–S–H gels that are formed because of the pozzolanic reaction of silica and alumina of pozzolana with the calcium hydroxide produced by the hydration of Portland cement is one of the main reason behind the technical benefits in the use of pozzolans with Portland cement in concrete. Previous studies (Thomas et al. 2012) have reported that smaller particle sizes and larger surface areas are beneficial to a faster cement hydration. The addition of biochar influences many properties like workability, rheology, entrapped air, setting time, hydration rate and released heat, microstructure and mechanical properties etc.

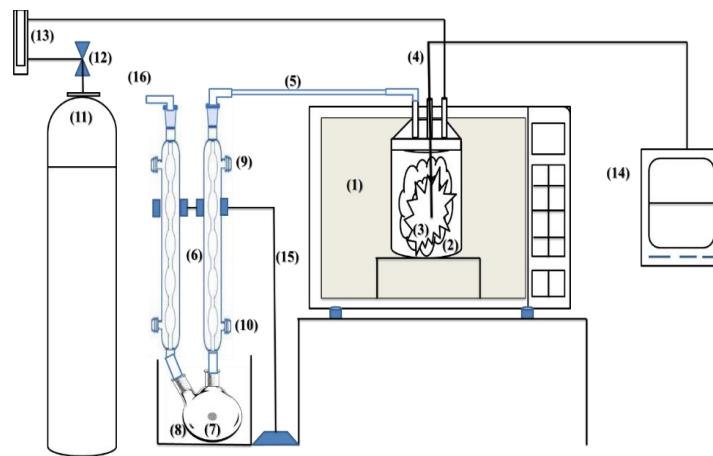
The replacement of cement by biochar depends on the content of silica and its chemical reaction with the cement compounds. Biochar comes from the pyrolysis process in which the volatile matter mainly cellulose and polysaccharides are eliminated and it contains mainly lignin. Biochar has unique properties such as porous structure, large specific surface area, complex surface groups, and stable chemical composition (Weber and Quicker 2018). Though biochar contains the components those have pozzolanic characteristics, no single index has yet been established to characterize the reactivity of biochar fully that can be relied. The effect of BC on the hydration of Portland cement is highly dependent on the specific surface area and mineral composition, which is controlled by the great variability of the raw stocks and pyrolysis conditions (Dixit et al. 2019). This is why the reactivity evaluation is an important parameter to determine whether biochar has the capacity to be pozzolanic or cementitious.

Biochar is regarded as a new kind of renewable and ecofriendly material having potential for use in future with its physicochemical properties coupled with its accessibility, low cost. The objective of this work is to study the feasibility of biochar to be used as a partial supplement of cement to be used in concrete and to investigate the properties for its suitable use.

Experimental investigation

Rice straw collected from paddy fields is sundried for 15 days to reduce the moisture content. The straw was shredded mechanically to less than 10 mm size. The shredded particles were converted to biochar in pyrolysis process that is heating in absence of air. As shown in the schematic diagram (Fig. 1), the volatile part is allowed to escape which are converted to syngas and biofuel and the residue left is the biochar. To get higher amount of biochar as compared to bio oil and syngas, a slow heating rate (0.1 to 1.0 °C/sec rise in temperature) with peak temperature in the range of 300°C to 500°C is maintained. The biochar produced was

grounded to make it powder form. The particle size distribution as presented in Fig. 2 shows that biochar is finer than the cement particles. The specific surface area and particle size distribution of pulverized BC particles are critical to the properties of BC-cement concrete. Previous studies (Thomas et al. 2012) have reported that smaller particle sizes and larger surface areas are beneficial to a faster cement hydration. The chemical composition of biochar is presented in Table -1 and compared with that of cement and flyash. The amorphous silica in the rice straw biochar can react with $\text{Ca}(\text{OH})_2$ in the secondary hydration to form a kind of C-S-H (calcium silicate hydrate)gel. The formation of the additional C-S-H contributes to both strength development and enhanced durability of concrete/mortar.



1- Microwave cavity	7- Bio-oil collector	13- Nitrogen flowmeter
2- Quartz reactor	8- Water bath	14- Temperature controller
3- Biomass sample	9- Water inlet	15- Holder
4- Thermocouple	10- Water outlet	16- Gas outlet
5- Glass connection	11- Nitrogen cylinder	
6- Condensers	12- Regulator	

Fig. 1 Schematic diagram of pyrolysis

Percentage chemical composition	Biochar (tested in laboratory)	OPC 53 grade cement (collected from literature)	Flyash (collected from literature)
CaO	7.58	60 - 65	5 - 25
SiO ₂	46.51	25 - 30	40 - 60
SO ₃	5.31	2-4	3 - 7
Inert carbon	35.24	--
Others	5.36	10 - 15	10 - 20

Table -1 Major components in biochar, cement and flyash

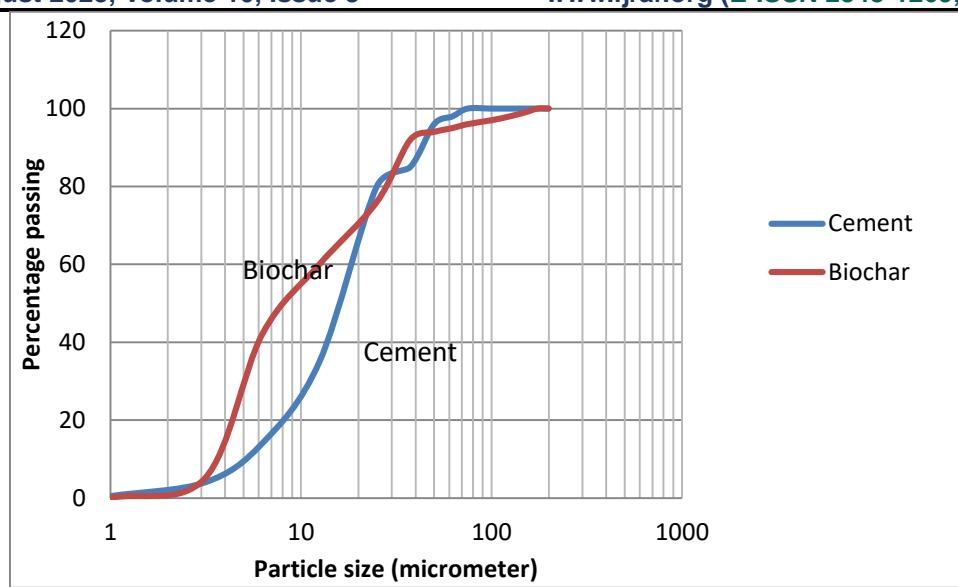


Fig. 3 Particle size distribution of cement and biochar

Preparation of concrete mix with biochar

The role of biochar in cement concrete was studied by comparing some properties with conventional concrete and those of concrete with different proportion of biochar in it. The reference concrete was prepared with OPC 53 grade cement, water cement ratio maintained at 0.4 and proportion of cement, sand and aggregates as 1:1.4:2.2 by weight for getting a M30 grade concrete. Experiments were then conducted for biochar added concrete with different proportion of biochar. The percentages of biochar added to concrete were 2.5%, 5% and 7.5% with respect to the weight of cement and it is blended with cement before mixing cement with aggregates for preparing concrete. Setting time, workability, compressive strength, split tensile strength and permeability tests were conducted.

Results and discussion

The effect of biochar was investigated both in the fresh and hardened concrete. The setting time of cement and slump value of concrete were investigated to observe the feasibility of use of biochar so that workability is not reduced that may make the concrete difficult or unfit for use in the construction stage. As observed, the setting time of cement and slump value of concrete decreases with increase of biochar percentage. This reduction is mainly due to the higher specific surface area of biochar as compared to cement. As observed from Fig. 3, while about 50% particles of cement are finer than 20 micron, it is around 72% for biochar. This indicates that the surface area of the constituent particles rises significantly and it needs more water for lubrication. Further, the water is absorbed by the porous structure of carbonaceous particles of biochar. This has been also observed by Choi et al. (2012) while studying the fluidity of biochar added cement slurry. Shortening of setting time is the result of filler effect and reduction of free water due to presence of carbonaceous particles. Some investigators (Restuccia et al. 2017) are of the opinion that that fine biochar particles act as seeds for cement hydration producing an earlier generation of cement hydration products.

Property	Concrete with 0% biochar	Concrete with 2.5% biochar	Concrete with 5.0% biochar	Concrete with 7.0% biochar
Initial setting time (minutes)	59	57	54	49
Final setting time (minutes)	207	204	195	175
Slump value (mm)	98	90	89	86

Table - 2 Setting time and slump value with different proportion of biochar in concrete

Strength	Compressive strength (N/mm ²)			Split tensile strength (N/mm ²)		
	7 day	14 day	28 day	7 day	14 day	28 day
Concrete 0% biochar	33.45	37.48	43.08	2.80	3.69	3.96
Concrete 2.5%biochar	34.26	38.79	45.32	2.91	4.04	4.58
Concrete 5.0%biochar	36.71	42.11	48.78	3.25	4.29	4.69
Concrete 7.5%biochar	31.64	35.03	41.47	2.59	3.21	3.32

Table – 3Strength of concrete with different proportion of biochar in concrete

The compressive strength of cement concrete mixed with biochar is affected by water-cement ratio, biochar dosages and curing conditions. Optimizing the dosage of biochar enhances the mechanical properties. It is observed that both compressive and tensile strength increase with increase in biochar percentage till about 5% replacement but decrease beyond that. This is because the carbonized particles of biochar absorb the water at the early stage of mixing and at after a certain limit complete densification of concrete is hampered and it reduces the strength with further increase of biochar. This can be improved with addition of a plasticizer. The required amount of moisture for hydration also falls that inhibit the strength inside the concrete.

Concrete (28day)	Permeability (x10 ⁻¹⁰ cm/sec)
Concrete with 0% biochar	0.260
Concrete with 2.5% biochar	0.233
Concrete with 5.0% biochar	0.218
Concrete with 7.5% biochar	0.209

The permeability is a parameter that is used to evaluate the resistance of concrete to prevent intrusion of external corrosive ions such as chlorides and sulphates. As observed, the permeability of concrete reduces with replacement of cement with biochar and this trend continues with more replacement of cement. This is due to two reasons. The pore space is filled up with finer biochar particles and the amorphous silica in the rice straw char react with $\text{Ca}(\text{OH})_2$ in the secondary hydration reaction to form the C-S-H (calcium silicate hydrate)gel. The formation of the additional C-S-H contributes to block the interconnection of path among the pores resulting lower permeability.

Conclusion

As observed, the cementitious properties of biochar help to replace cement to around 5% by weight of cement consumed. It not only adds to the strength but has an advantageous use in making concrete impermeable which also helps in reducing the corrosion of the embedded steel. The idea of using an agricultural waste material that is harmful for the atmosphere during its burning can be utilized in a better way.

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