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Geopolymer concrete with ground granulated blast furnace slag and black rice husk ash

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Original scientific paper

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Geopolymer concrete with ground granulated blast furnace slag and black rice husk ash

An experimental study on the strength and durability properties of geopolymer concrete prepared using the ground granulated blast furnace slag and black rice husk ash is presented in the paper. The geopolymer concrete was initially prepared with ground granulated blast furnace slag as the primary binder instead of cement, and then blast furnace slag was replaced with black rice husk ash. The addition of more than 10 % of black rice husk ash in geopolymer concrete retards the strength development, although such strength values are still above the target strength for up to 20 % replacement levels.

Key words:

geopolymer concrete, blast furnace slag, black rice husk ash, strength, chloride permeability, accelerated corrosion

Izvorni znanstveni rad

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Geopolimerni beton s dodatkom granulirane zgure i crnog pepela rižinih ljuški

U radu je prikazano eksperimentalno istraživanje čvrstoće i trajnosti geopolimernog betona s granuliranim zgurom visokih peči i crnim pepelom rižinih ljuški. Geopolimerni beton je prvo bitno pripremljen s granuliranim zgurom kao primarnim vezivom umjesto cementa, a zatim je zgura zamijenjena s crnim pepelom rižinih ljuški. Dodatak crnog pepela u geopolimernom betonu iznad 10 % usporava razvoj čvrstoće, ali su takve vrijednosti čvrstoće i dalje iznad ciljane sve dok dodatak crnog pepela u betonu ne prelazi 20 %.

Ključne riječi:

geopolimerni beton, zgura visokih peči, crni pepeo rižinih ljuški, čvrstoća, propusnost klorida, ubrzana korozija

Wissenschaftlicher Originalbeitrag

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Geopolymerbeton mit granulierter Hochofenschlacke und schwarzer Reisschalenasche

In dieser Arbeit werden experimentelle Untersuchungen zur Festigkeit und Beständigkeit von Geopolymerbeton mit granulierter Hochofenschlacke und schwarzer Reisschalenasche (eng. Black Rice Husk Ash) dargestellt. Die Betonmischung wurde zunächst so zubereitet, dass granulierte Hochofenschlacke als Hauptbindemittel anstelle von Zement eingesetzt wurde. Ein Anteil an Reisschalenasche über 10% führt zu einer langsameren Festigung des Geopolymerbetons, aber die Festigkeit überschreitet trotzdem den gezielten Werten, solange dieser Anteil nicht höher als 20 % ist.

Schlüsselwörter:

Geopolymerbeton, granulierte Hochofenschlacke, schwarze Reisschalenasche, Festigkeit, Chlorid-Permeabilität, beschleunigte Korrosion

1. Introduction

The Ordinary Portland Cement (OPC), whose production has a severe environmental impact, is the principal ingredient of concrete. Cement production contributes with about 7 % to the overall global greenhouse gas emission [1]. The production of one tonne of the OPC requires 4GJ of energy, and also emits about one tonne of carbon dioxide into the atmosphere [2]. Also, raw materials required for cement production are non-renewable, and are depleting at a rapid rate. At the same time, a lot of industrial and agro wastes with inherent cementitious properties are produced abundantly, but are mostly dumped into landfills. Employing such by-products as alternates for cement has manifold benefits including conservation of environment, sustainability of resources, and solution to the by-products disposal problem. Extensive research is being carried out to assess the feasibility of utilizing industrial wastes as competent replacement for OPC, and for generating superior binders. One such successful attempt is geopolymers concrete, which entirely eliminates the use of OPC in concrete production.

Joseph Davidovits coined the term "geo-polymer" in 1978 to describe a family of mineral binders that possess a chemical composition similar to zeolites while exhibiting an amorphous microstructure. In contrast to OPC, principal binders in geopolymers concrete are not calcium-silicate-hydrates (CSHs). Instead, the role of binder is assumed by an aluminosilicate polymeric gel, formed by the tetrahedrally-bonded silicon and aluminium with oxygen atoms shared in between [3]. Two important constituents of geopolymers concrete are source materials and alkaline liquids. The source materials must be rich in silicon (Si) and aluminium (Al). These could be either natural minerals like kaolinite, clays, etc. or by-products like fly ash, blast furnace slag, silica fume, rice-husk ash, etc. The alkaline liquids are based on soluble alkali metals, most frequently sodium or potassium. The most common alkaline liquid used is a combination of sodium or potassium hydroxide along with the sodium or potassium silicate, correspondingly. The Black Rice Husk Ash (BRHA) is an agro-industrial waste generated in the rice milling industry. It is obtained by burning rice husk in incinerator. The ash obtained as a result of this combustion process has a high content of unburnt carbon [4]. Hence the use of BRHA as a building material is very limited, even though it has a high silica content of about 87-97 % [5]. But several researchers including Chatweera and Lertwattanarak (2011) and Piyaphanuwat and Asavapisit (2009) reported that the addition of BRHA in concrete has improved its durability properties [6, 7]. In geopolymers concrete, most of the research work has focused on fly ash based binders. However, in the present study, the industrial waste, namely the Ground Granulated Blast furnace Slag (GGBS), and the agro waste, namely the Black Rice Husk Ash (BRHA), are used as source materials for geopolymers concrete. The GGBS was kept as the base material in which the BRHA was added in different

percentages, and its effects on the compressive, flexural and tensile strengths, and durability properties, like chloride permeability and resistance to accelerated corrosion, were studied.

2. Materials used

2.1. Ground granulated blast furnace slag (GGBS)

The GGBS was obtained from JSW cements limited, Bellari, India. The chemical composition of GGBS given by SGS India Pvt. Ltd. Laboratory, Chennai India is given in Table 1.

Table 1. Properties of GGBS and BRHA

Property	GGBS	BRHA
SiO ₂	31.25 %	93.96 %
Al ₂ O ₃	14.06 %	0.56 %
Fe ₂ O ₃	2.80 %	0.43 %
CaO	33.75 %	0.55 %
MgO	7.03 %	0.4 %
Loss on ignition	1.52 %	9.79 %
Specific gravity	2.61	2.14
Blaine fineness	4550 cm ² /g	5673 cm ² /g

2.2. Black rice husk ash (BRHA)

The BRHA was obtained from a local rice mill. It was finely ground in a ball-mill for 30 minutes and passed through a 75µm sieve [8]. The Chemical composition of BRHA, given by SGS India Pvt. Ltd. Laboratory, Chennai, India is, given in Table 1.

2.3. Fine aggregate

Natural river sand conforming to Zone II as per IS 383 (1987) [9], with a fineness modulus of 3.45 and a specific gravity of 2.6, was used.

2.4. Coarse aggregate

Crushed granite coarse aggregate conforming to IS: 383 (1987) [9] was used. Coarse aggregate of size 20 mm and below with a specific gravity of 2.87, and fineness modulus of 8.14 was used. The aggregates were tested as per IS 2386 (1963) [10].

2.5. Alkaline solution

A mixture of sodium hydroxide and sodium silicate was used as the alkaline solution. The commercial grade sodium hydroxide in form of pellets (97 %–100 % purity), and sodium silicate solution having 14.7 % of Na₂O, 29.4 % of SiO₂, and 55.6 % of water by mass, were used. The molar concentration of sodium hydroxide



Figure 1. Materials for geopolymer concrete: a) GGBS; b) BRHA; c) mixture of sodium hydroxide and sodium silicate

was kept as 8M and the ratio of sodium silicate to sodium hydroxide was taken to be 2.5.

2.6. Superplasticizer

A high-range water-reducing naphthalene based superplasticizer was used to improve the workability of fresh concrete.

2.7. Water

Extra water in the amount of about 15 % of the binder content was added to increase the workability of the concrete.

3. Mix proportions

Since no code provisions are available for the mix design of geopolymer concrete, the density of geopolymer concrete was assumed to be 2400 kg/m³, and other calculations were made based on the density of concrete as per the design proposed by Lloyd and Rangan (2010) [11]. The combined total volume occupied by the coarse and fine aggregates was assumed to be 77 %. The alkaline liquid to binder ratio was taken to be 0.40. The target strength of 40 MPa was fixed as for a regular strength concrete. The mix proportions are given Table 2.

Table 2. Mix proportions of geopolymer concrete

Mix	GGBS [kg/m ³]	BRHA [kg/m ³]	Coarse aggregate [kg/m ³]	Fine aggregate [kg/m ³]	Sodium hydroxide [kg/m ³]	Sodium silicate [kg/m ³]	Super-plasticizer [%]	Water [l/m ³]
GP	394	0	1201	647	45	113	1,5	59
GPR1	355	39	1201	647	45	113	1,5	59
GPR2	315	79	1201	647	45	113	1,5	59
GPR3	276	118	1201	647	45	113	1,5	59

Note: GP - Control concrete, GPR1 - mix with 10 % BRHA, GPR2 - mix with 20 % BRHA, GPR3 - mix with 30 % BRHA

4. Preparation of test specimens

The materials for the mixes were weighed and first mixed in dry condition for 3-4 minutes. Then the alkaline solution, which is a combination of sodium hydroxide and sodium silicate, and the super-plasticizer, were added to the dry mix. Extra water in the quantity of about 15 % by weight of the binder was added to improve the workability. The mixing was continued for about 6-8 minutes. The concrete was placed and compacted in steel moulds. After casting, the moulds were placed in the oven where they were dried at 60 °C for 8 hours. Then the specimens were taken out and removed from their moulds. After that, they were additionally cured in the oven for another eight hours. Then the specimens were taken out and allowed to cure at room temperature until the day of testing.

5. Tests conducted

5.1. Compressive strength test

The compressive strength of the geopolymer concrete was tested as per IS 516:1959 [12]. Cube specimens 150 mm in size were cast for each proportion and tested for their compressive strength at the ages of 3, 7 and 28 days. All the specimens were

tested using the Compression Testing Machine (CTM) 2000 kN in capacity under a uniform rate of loading of 140 kg/cm²/min until failure, and the ultimate load at failure was registered to enable calculation of compressive strength.

5.2. Split tensile strength test

The split tensile strength test was carried out as per IS 5816:1999 [13]. Cylindrical concrete specimens 150 mm in diameter and 300 mm in height were cast. The specimens were then tested to determine the splitting tensile strength using a Universal Testing Machine (UTM) at the ages of 3, 7 and 28 days.

5.3. Flexural strength test

The flexural strength of the geopolymer concrete was carried out as per IS 516:1959 [12]. Beams measuring 150 mm × 150mm × 700 mm were cast and then subjected to the flexural strength test using a Universal Testing Machine (UTM) at the ages of 3, 7, and 28 days.

5.4. Rapid chloride permeability test

The Rapid Chloride Permeability Test (RCPT) was conducted in accordance with ASTM C1202-97 [14]. This test is a rapid measurement of electrical conductance of concrete with respect to its resistance against chloride ion penetration. Cylindrical specimens 95 mm in diameter and 50 mm in thickness were used for this test after 28 days from the date of casting. A potential difference of 60 V was maintained across the ends of the specimen for about 6 hours. One end was mounted to a cell containing 3 % of sodium chloride solution, and the other end was mounted to a cell containing 0.3 N of sodium hydroxide solution. The current passing through the specimen was measured for every 30 minutes until 6 hours. The chloride contamination and temperature were also monitored. The total charge passing through the specimens was calculated in coulombs based on the current and time values, and then this charge was related to the resistance of specimens against chloride ion penetration. The greater the total charge, the higher the permeability of the specimen.

5.5. Accelerated corrosion test

The accelerated corrosion test was conducted on cylindrical specimens 100 mm in diameter and 200 mm in height, with a 14 mm diameter steel rod embedded centrally so that an equal cover was maintained at all sides. The specimens were oven cured at 60 °C for 16 hours after casting, and were then further cured at room temperature for 28 days. The cylindrical specimens were then placed in individual containers, each containing a 4 % sodium chloride solution. The level of the solution was maintained at 75 mm from the bottom of the specimen throughout the test. A stainless steel plate placed in each container acted as the cathode

whereas the steel rod embedded in concrete served as the anode. They were connected to a constant DC supply of 6V so that the setup acted as an electrochemical cell. The constant voltage was maintained throughout the test and the current passing through each specimen was measured on a daily basis. At the appearance of first crack on each specimen, the current supply was switch off and the specimens were removed from the test setup. Once the test was completed for all the specimens, a graph was plotted for the current passed in mA versus time in days to determine the corrosion initiation and propagation periods. The test setup is shown in Figure 2.



Figure 2. Accelerated corrosion test setup

6. Results and discussion

6.1. Compressive strength

The compressive strength test results obtained for geopolymer concrete at 3, 7 and 28 days are shown in Table 3.

Table 3. Compressive strength of geopolymer concrete

Mix	Compressive strength [MPa]		
	3 days	7 days	28 days
GP	60.9	66.5	69.28
GPR1	62.3	67.6	70.72
GPR2	44.72	46.32	51.46
GPR3	19.24	20.48	24.52

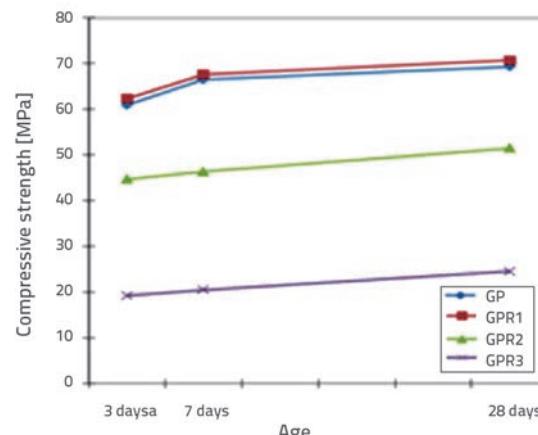


Figure 3. Compressive strength values for geopolymer concrete with different BRHA Content

Figure 3 represents the compressive strength variation for specimens.

The effect of BRHA on the compressive strength of geopolymer concrete is discussed. Geopolymer concrete made with 100 % GGBS was kept as the control specimen. There is a small increase in compressive strength for the 10 % BRHA replacement, which is comparable to that of the control mix. A higher temperature during oven curing enables greater dissolution of Si and Al ions and thus the formation of a stronger polymer chain as mentioned by Kusbiantoro et al. [15]. The rest of the mixes showed lower compressive strength compared to that of the control specimen. The addition of silica rich BRHA increased the unreactive silica content i.e., increasing the Si/Al ratio which inhibited the geopolymer reactions in spite of temperature increase as reported by Duxon et al. [16]. It can however be seen that the BRHA added geopolymer concrete did exceed the target strength of 30 MPa and attained substantial 28th day strengths of around 70.72 MPa for the 10 % addition and 51.46 MPa for the 20 % BRHA. The 30 % BRHA added specimens did not achieve any significant strength.

6.2. Split tensile and flexural strengths

The splitting tensile and flexural strength results for geopolymer concrete at 3, 7, and 28 days are given in Table 4, and the variation of the split tensile strength and flexural strength values for various mixes is shown in Figure 4 and Figure 5, respectively.

Table 4. Split tensile and flexural strength values

Mix	Split tensile strength [MPa]			Flexural strength [MPa]		
	3 days	7 days	28 days	3 days	7 days	28 days
GP	6.16	6.43	6.74	5.13	5.75	6.06
GPR1	6.47	6.69	6.92	5.69	6.26	6.98
GPR2	3.72	3.94	4.26	3.18	3.57	4.12
GPR3	0.81	0.89	1.12	0.91	1.05	1.27

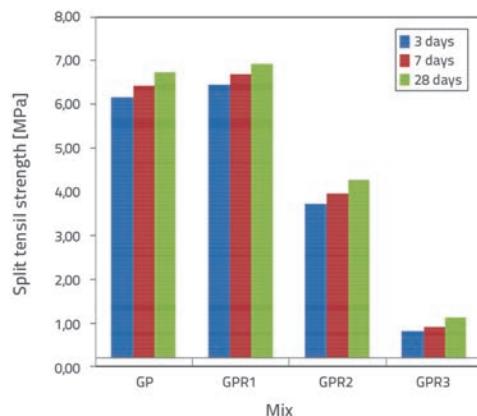


Figure 4. Split tensile strength of geopolymer concrete

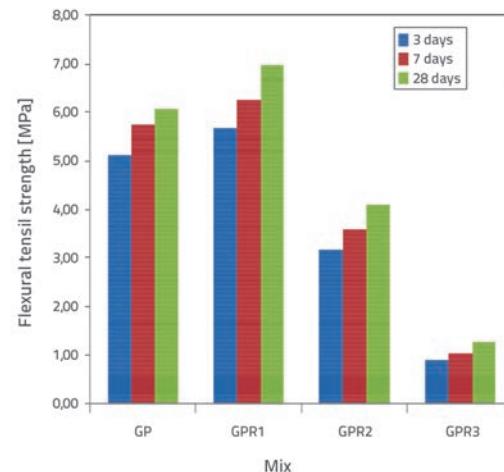


Figure 5. Flexural tensile strength of geopolymer concrete

When comparing the 10 % BRHA replaced mix GPR1 with the control mix GP, it can be seen that there is a slight improvement in both the split tensile and flexural strength values. The heat curing of the specimens, along with an increased $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and higher fineness of BRHA particles, might have assisted the dissolution of ions and the poly-condensation mechanism of the geopolymer framework. But the split tensile and flexural strength values seem to decrease with a further increase in the BRHA content. Similar results were reported by Jing Liu et al. [17] with regard to the use of the palm oil fuel ash as a geopolymer concrete binder. BRHA particles possess a different silicate structure and, when the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio exceeds a very high value, the kinetics of the polymerization mechanism is inhibited and the production rate of geopolymer gel is reduced as revealed by Kusbiantoro et al. [15].

6.4. Rapid chloride permeability test (RCPT)

The rapid chloride permeability test results at 28 days for the geopolymer concrete mixes are given in Figure 6.

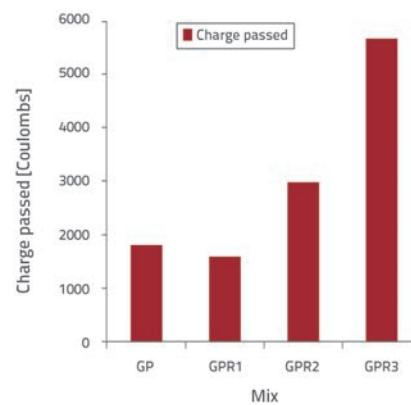


Figure 6. RCPT of geopolymer Concrete

The total charges for the control, 10 %, 20 %, and 30 % BRHA replaced specimens in terms of Coulombs amount to 1813.2,

1597.5, 2977.5 and 5675.1, respectively. There is a reduction in the charge passed for the 10 % BRHA replaced specimen when compared to the control specimen. Then it tends to increase with a further addition of the BRHA. As per classification given in ASTM C1202 [14], the charges passed through the specimens classify the chloride penetrability as low for the control specimen and the 10 % BRHA replaced specimens. It is moderate for 20 % and high for 30 % BRHA replacement levels respectively. One of the key factors influencing the concrete permeability is the pore structure. The BRHA replacement at an optimum level reduces the chloride ion penetration, which is characterized by the micro filler effect of the fine BRHA particles. The fine BRHA particles arrest the pores and result in a more compact concrete structure thereby reducing the liquid penetration property, as inferred by Sampaio et al. [18]. However, as the BRHA is rich in silica, its excessive addition leads to an inappropriate $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. This affects the structural compactability of the geopolymer causing a higher ion transport through concrete.

6.5. Accelerated corrosion

The variation of current passed through the specimens in mA with time in days is shown in Figure. 7.

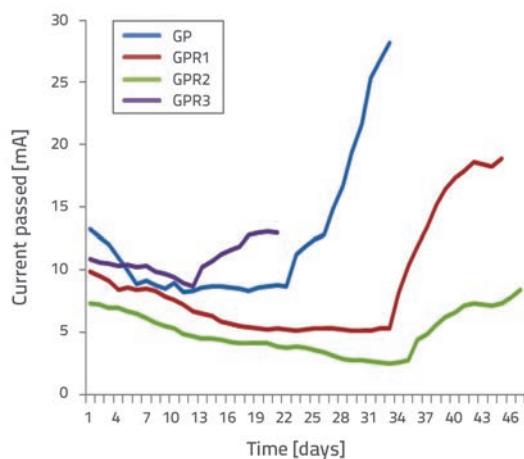


Figure 7. Variation of current over time

It can be seen that the current profile is steady in the beginning, and that it declines with time. This is due to the formation of a passive layer by the geopolymer matrix, which delays the effect of the applied voltage to accelerate the corrosion process. This has been confirmed by Olivia and Nikraz [19]. After a certain period of time, the current suddenly increases. This particular point in time is called the corrosion initiation period, which signifies the onset of the corrosion process in concrete. The migration of chloride ions increases with time and, once it reaches the critical chloride content of the steel bar used, it results in de-passivation, as reflected by a sudden increase in current. The initiation period for the control concrete is 23 days and the specimen showed first crack at the 33rd day. For the 10 % BRHA replacement, the initiation period is increased

to 34 days, and the first crack was observed at the 45th day. The initiation period is 36 days for the 20 % BRHA replacement, where the first crack was observed at the 47th day. For the 30 % BRHA replacement, the initiation period is reduced to 13 days and the specimen showed its first crack at the 23rd day. It is evident from the results that an optimum BRHA addition increases the corrosion initiation period while delaying cracking. Fine BRHA particles facilitate an effective dissolution of silica and alumina ions and formation of a stronger geopolymer matrix. Subsequently, they account for the development of a more resistive passive layer countering the attack of chloride ions. However, an excessive BRHA content has a negative effect on corrosion prevention as it retards development of a stronger geopolymer matrix and, as a result, the passive layer around the reinforcement is weakened.

7. Conclusions

The experimental results show that it is possible to produce geopolymer concrete of substantial strength and durability using GGBS and BRHA. The following conclusions can also be derived from the present study:

- The addition of BRHA beyond 10 % had a retarding effect on the compressive strength. At up to 20 % replacement, the target strength was surpassed and compressive strength as high as 51 MPa was reached at 28 days. The split tensile and flexural strengths showed a trend similar to that of the compressive strength with respect to the BRHA proportion.
- The geopolymer concrete specimens showed good resistance to chloride permeability. The chloride permeability level was low for the 10 % BRHA and moderate for the 20 % BRHA.
- The incorporation of BRHA in geopolymer concrete increases its corrosion resistance. The corrosion initiation period was 34 days for the 10 % BRHA and 36 days for the 20 % BRHA, while it was only 23 days for the control specimen. It is possible that the fine BRHA particles account for greater dissolution of silica and alumina ions and a stronger passive layer formation.
- The addition of BRHA beyond 20 % is not beneficial for geopolymer concrete. The 30 % BRHA replaced specimens neither achieved significant strength nor proved durable.

The strength results show that an optimum proportion of BRHA that can be used in geopolymer concrete is 20 %, considering the target strength of 30 MPa. It can be seen from the durability studies that the geopolymer concrete performed remarkably well with regard to chloride penetration and corrosion resistance for up to 20 % BRHA replacement. These results are very important for the development of such innovative concretes, in which the use of OPC is completely omitted. It promotes the utilization of alternate materials like GGBS and BRHA for binder production. Since these materials are essentially industrial by-products, it also means a solution to their disposal problem.

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