BIOGENIC TREATMENT IMPROVES THE DURABILITY OF STEEL SLAG AMENDED MORTAR STRUCTURES

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ABSTRACT

Steel slag is an industrial waste that is generated during the production of steel. Steel slag is a calcium-rich heterogenous solid consisting of several solid phases. Presence of high contents of free-CaO in steel slag endorses its cementitious property and makes it a potential candidate for alternate supplementary cementitious material. The usage of slag as a construction material is hindered by its volume instability due to its carbonation. In the present investigation, *Staphylococcus pasteurii* strain isolated from steel slag was tested for its ability to improve the durability properties of steel slag amended mortar specimens. In replacement of fine aggregate with steel slag (30% and 50%) along with microbial treatment, significant increase in compressive strength (28%) and reduction in permeability (8 times) was observed in 30% slag amended mortar specimen as compare to control. Hence, microbial treatment along with steel slag usage in building materials provides an efficient way to enhance its properties as well as diminish environmental related concerns.

Key Words: Microbial concrete; Steel slag; Urease; Water absorption; Compressive strength; Calcium carbonate

INTRODUCTION

In the current scenario of urbanization and industrialization, infrastructure of a country plays an important role. In all the infrastructure categories, concrete is the most widely used construction material. With the continued demand, world without concrete is hard to imagine. In simplest form of definition concrete is a mixture of sand, aggregates, cement and water. Among these components of concrete, cement is the most important ingredient which acts as a binder material. Globally, production of cement has been escalated by cement companies to meet the requirement of construction projects. Emerging economies such as India and China are developing their infrastructure at a rapid pace. The cement production is a highly intensive energy consuming as well as a major CO_2 emitting process (Worrell et al., 2001). It was reported that the total emissions in the industrial production of cement contributes 8% of global CO_2 emissions (Andrew, 2018). The cement industry faces challenges to reduce global CO_2 emissions and effectively contribute to sustainable development (Imbabi et al., 2012). In recent years, to address the environmental impact associated with cement production, researchers began to design new binders by partially replacing ordinary Portland cement (OPC) with supplementary cementitious materials (SCMs)

(Juenger and Siddique, 2015; Aprianti, 2017). Developments in producing sustainable concrete by substituting cements or natural aggregates with waste by-products such as flyash, silica fumes, spent foundry sand, geopolymers and steel slag are reported (Chindaprasirt et al., 2007; Shi and Qian, 2003; Pedro et al ., 2017; Torres et al., 2017; Siddique et al., 2018; Singh et al., 2015; Tsakiridis et al., 2008; San-José et al., 2014). Large scale production of these by-products may lead to release of substantial amount of hazardous wastes due to improper disposal (Misra and Pandey, 2005). The use of such by-products in construction materials will not only be beneficial in minimizing the cost of construction but also helps in environment protection. Reusing the large volume of by-product in cement industry will contribute in sustainable development and reduce the problem of landfilling.

Among all the industrial waste products, steel slag is the fastest generated by-product produced from steel making industry. Global production of steel slag according to US Geological Survey was reported to be in order of 170 million to 250 million tons (Mo, 2018). Steel slag primarily consists of oxides of calcium, silicon, iron, magnesium, aluminum and small amounts of heavy metals. Presence of C_3S, C_2S, and C_2F in steel slag endorses its cementitious property (Shi, 2004). Effect of using steel slag in concrete research has been carried out by many researchers to improve the physical and chemical properties of concrete (Wang et al., 2013; Manso et al., 2006; Sorlini et al., 2012; Rosales et al., 2017; Maes et al., 2013). Various studies have reported that steel slag can act as a potential cement additive and concrete admixture with proper replacement (Yüksel, 2017). Instead of improved mechanical properties in steel slag amended concrete, volume expansion in structures also contributes disintegration as the time goes (Le et al., 2017). Due to the presence of excessive free (un-hydrated) lime (f-CaO) and periclase (f-MgO) in slag, hydration causes volume instability. Hydration of free-CaO and MgO into hydroxide form increases the solid volume which further gives rise to microcracking (Brand and Roesler, 2015). To stabilize the effect of volume expansion, suitable methods must be adopted. Pretreatment of slag by leaving it in outdoor environment for months was reported to decrease free-CaO content from 1.20% to 0.61% (Le et al., 2017). To avoid open disposal in land and lengthy processing time, carbonation technique to stabilize slag is also reported (Mo, 2018).

In regard to sustainable developments in improving the durability properties of concrete, application of biomineralization in cement-based materials has become substantially popular. It is a microbial-based strategy in which concrete structures are treated with calcifying bacteria to induce calcium carbonate precipitation (Joshi et al., 2017). During the last decade, number of researchers had reported the potential of microbial induced calcium carbonate precipitation (MICP) in durability enhancement of concrete structures (Reddy and Joshi, 2018). MICP in a construction material can be made by supplementing ureolytic bacteria with calcium source along with urea (Joshi et al., 2018). The mechanism for MICP is described by the reactions:

$$CO(NH_2)_2 + 2H_2O \xrightarrow{\text{Bacteria}} 2NH_4^+ + CO_3^{2-}$$

$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3\downarrow$$
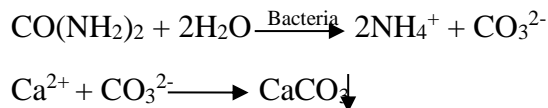
In the context of steel slag amended mortar or concrete, previous studies mainly addresses the replacement of cement or aggregates with optimum levels of steel slag. In the present study, steel slag amended cement mortar will be treated with calcifying bacterial strain, isolated form steel slag. Current study also explores the feasibility of microbial stabilization of steel slag with the

isolated bacterial strain. This research work evaluated the change in compressive strength, water absorption and microstructural analysis of microbial treated steel slag mortar.

MATERIALS AND METHODS

Sample Site
Steel slag samples were collected from Tata Steel Industries, Jamshedpur, India. Sample was sieved through predetermined sieve size of 4.75 mm and used for the isolation of calcifying bacteria.

Isolation and Identification of Calcifying Bacteria
For the isolation of bacteria involved in calcium carbonate ($CaCO_3$) precipitation, 2 g of steel slag sample was added in 100 mL nutrient broth (Hi-Media, Mumbai, India) (pH 8.0) containing 2% urea and incubated at 37°C for 120 hrs at 120 rpm. For isolation and enumeration of bacteria, the sample was serially diluted in saline (0.85% NaCl) and plated on urea agar base medium and incubated at 37°C overnight. Intensity of pink colored halo zone around colonies indicated urease enzyme production. These colonies were selected for quantitative estimation of urease enzyme. For estimation of urease activity in urease positive isolates was determined according to phenol-hypochlorite assay (Achal et al., 2010). Efficient bacteria capable of precipitating $CaCO_3$ were identified based on 16S rRNA sequence analysis.

Estimation of Soluble Calcium Content
In order to stabilize the soluble calcium in slag by isolated bacterial strain, 1% inoculum of overnight grown bacterial culture in 100 ml autoclaved nutrient broth (NB) medium (Peptone 10 g/L, Yeast extract 10 g/L, Sodium chloride 5 g/L) was inoculated. It was supplemented with filter sterilized 2% urea along with 5 gm steel slag. Flask was incubated at 37°C in rotating shaker at 120 rpm for 144 hours. The aliquots from flask was taken at regular time intervals of 24 hours and the broth was centrifuged to quantify soluble Ca^{2+} in the supernatant by EDTA titration method (Dhami et al., 2016).

Biocementation in Slag Amended Cement Mortars
Cement mortar mix was prepared by using cement: sand in the ratio of 1:3 (by weight) and water to cement ratio (w/c) of 0.5. Cement and sand were thoroughly mixed for 2 min before adding water. To determine compressive strength and permeation properties, cube moulds of dimension (50 mm × 50 mm × 50 mm) were casted. For slag amended mortar, partial replacement of fine aggregate with slag (30% and 50%) was carried out. In bacterial treated slag mortars, partial replacement of fine aggregate was done along with grown bacterial culture. During casting, NB medium with bacterial culture ($OD_{600} = 0.5$) supplemented with 2% urea (w/v) was used instead of water. After 24 hours of casting, specimens were demoulded and cured till the testing age. Mix proportions of different sets of cube samples with different curing regimes are specified in Table 1 & 2 respectively.

Table 1. Mixture proportions of cement motar cubes (per 50 mm cube)

Composition		Control	Untreated		Bacterial Treated	
		C	30CS	50CS	30SBT	50SBT
Cement		76.2 g	76.2 g	76.2 g	76.2 g	76.2 g
Fine Aggregate		228.6 g	160.2 g	114.3 g	160.2 g	114.3 g
Slag	30% Replacement	-	68.58 g	-	68.58 g	-
	50% Replacement	-	-	114.3 g	-	114.3 g
Water		38.1 g	38.1 g	38.1 g	-	-
Bacterial culture		-	-	-	38.1 g	38.1 g

Table 2. Outline of different sets of mortar specimen and method of curing treatment

Specimen		Material	Method of curing
Control		Cement:Sand Water/Cement = 0.5	Water curing for 7 and 28 days
Cement-Steel Slag		Cement:Sand:Slag Water/Cement = 0.5	Water curing for 7 and 28 days
Cement-Steel slag & Bacterial treated	30% Replacement	Cement:Sand:Slag Bacterial culture/Cement = 0.5	Submersion in NBU medium and Bacterial culture for 7 and 28 days
	50% Replacement	Cement:Sand:Slag Bacterial culture/Cement = 0.5	Submersion in NBU medium and Bacterial culture for 7 and 28 days

NBU medium had the following concentration: Nutrient broth (Peptone 10 g/L, Yeast extract 10 g/L, Sodium chloride 5 g/L) and 2% Urea (w/v)

Test Procedures
To study the compressive strength, cement mortar cubes of 50 mm dimension was casted (BIS: 4031). Compressive strength of mortar cubes with/without steel slag and bacterial treatment were determined at the age of 7 and 28 days using an automatic compression testing machine, COMPTEST 3000.

Permeation properties of different mortar cubes as described in Table 1 were measured at 28 days of casting (Achal et al., 2011). For studying water absorption, all mortar samples were dried in oven at 60°C overnight and dry weight was measured (W_{oven} dried). To calculate the rate of water absorption of specimens exposed to 10 ± 1.0 mm of water were removed from the water and weighed at regular time intervals (15 min, 30 min, 1 h, 1.5 h, 3 h, 5 h, 8 h, 24 h, 72 h, 96 h, 120 h, 144 h and 168 h). The sorptivity coefficient k [cm $s^{-1/2}$] was calculated from the following expression $Q/A = k\sqrt{t}$.

Here, Q is the amount of water absorbed [cm^3]; A is the cross section of the cube which was in contact with water [cm^2]; t is the time [s]; Q/A is plotted against the square root of time, k is calculated from the slope of liner relation from these two.

To study the role of bacterial treatment in slag amended mortar, scanning electron microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX) was performed in mortar specimens at the curing age of 28 days

RESULTS AND DISCUSSION

Isolation and Identification of Calcifying Bacteria

Primary screening for the selection of efficient bacterial strain from steel slag sample a qualitative test for urease production in urea agar media was done. Based on the pink color intensity out of twenty-four bacterial colonies, six were selected and designated as PP1, PP4, PP6, PP8, PP9, and PP11. The selected bacterial isolates were subjected to quantitative analysis of urease productivity. Among all the isolates, PP9 significantly produced higher urease activity and selected for further studies (Fig. 1).
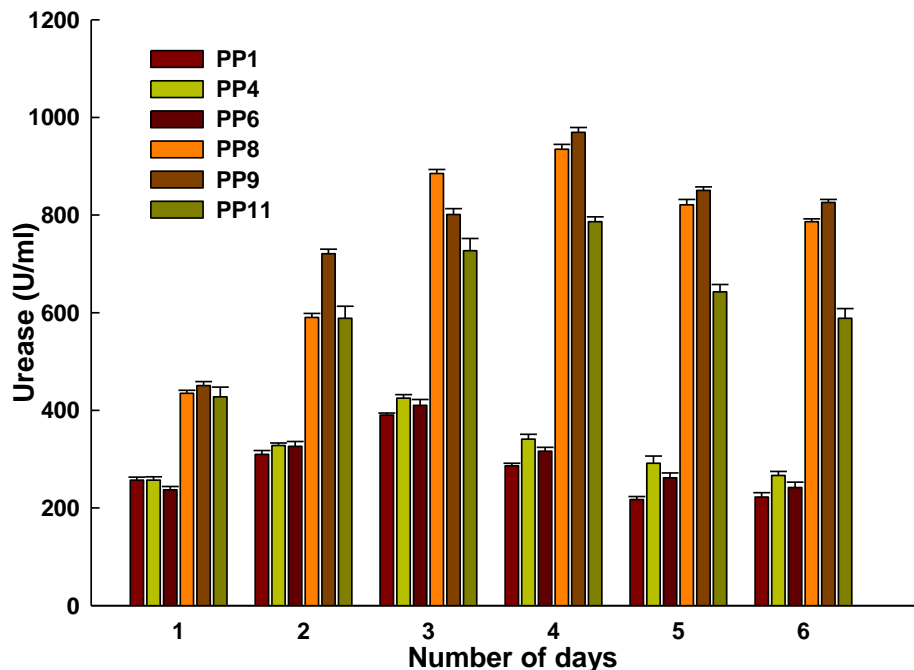

Fig. 1. Urease production (U/ml) by bacteria isolated from steel slag sample.

Since PP9 exhibited the maximum urease activity, it was considered for characterization subjected to 16S rRNA sequence analysis and was identified as *Staphylococcus pasteurii*. To study the pathogenicity of PP9, coagulase test and mannitol test were carried out and PP9 isolate was confirmed as nonpathogenic bacteria.

Estimation of Soluble Calcium Content

Soluble calcium content estimation by the bacterial isolate PP9 was evaluated at flask level by EDTA titration method. Initial readings of soluble calcium were noted to be the highest. The

soluble calcium content was found to decrease with time due to its consumption by calcifying bacteria (Fig. 2). This indicates the conversion of available free-CaO content into $CaCO_3$ precipitation as soluble calcium content is converted to $CaCO_3$ crystals by PP9.
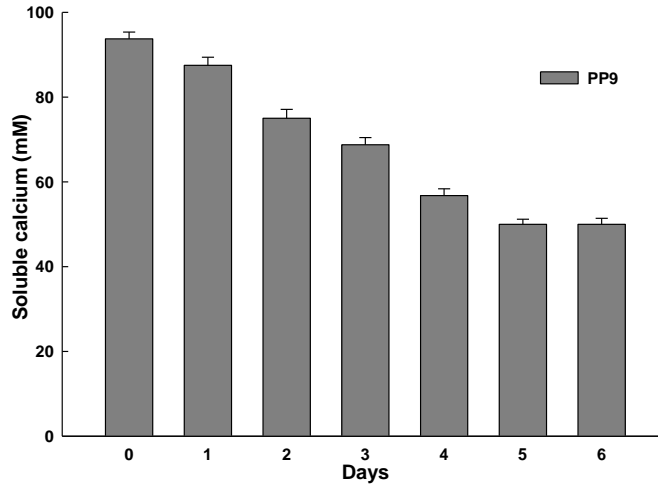

Fig. 2. Variation in soluble calcium content of medium inoculated with PP9

Mechanical and Permeation Analysis

Compressive Strength

Effect of bacterial treatment and slag replacement on compressive strength of mortar samples was monitored after 7 and 28 days curing (Fig. 3). Control specimen showed compressive strength value of 20.6 MPa and 24 MPa at the age of 7 and 28 days respectively. When compared to control, no significant change in strength was observed in 30CS and 50CS specimens after 7 days curing. However, after 28 days of curing 30CS and 50CS specimens showed an increase of 13.75% and 9.5% in compressive strength as compare to control. The bacterial treated specimens along with slag replacement showed notable change in strength. At the age of 28 days, it was observed that 28% increase in compressive strength of 30SBT specimen as compared to control.
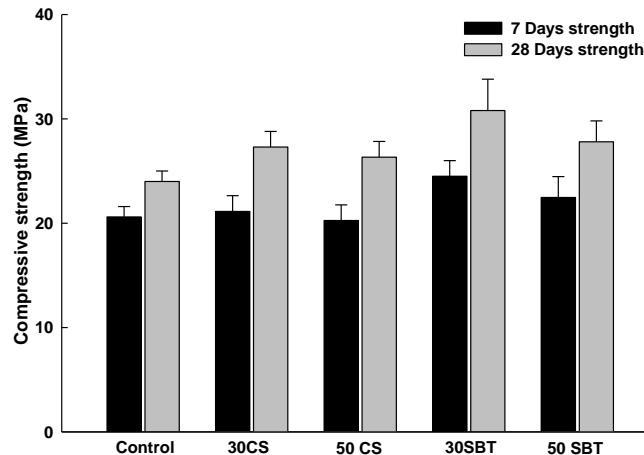
Fig. 3 Influence of steel slag and bacterial treatment on compressive strength (MPa) of mortar specimen

However, 50SBT specimen showed only 15% increase in strength when compared to control. It was observed that as the amount of steel slag replacement was increased from 30% to 50%, overall strength decreased. It was observed that the application of MICP technology along with 30% replacement of fine aggregates with steel slag improved the mechanical strength of 30SBT specimen. Due to dense biodeposition of calcium carbonate precipitation helped in densifying the mortar matrix. Similar observation of increased strength in microbial mineralized steel slag bricks due to deposition of $CaCO_3$ crystals was reported (Wang et al., 2016).

Water Absorption Test
Among all the specimens, control mortar has highest water absorption followed by 30CS and 50 CS specimens (Fig. 4). The specimens treated with bacteria either 30SBT or 50SBT registered significantly lowest water absorption as compared to control. It was concluded that the bacterially treated specimen 30SBT absorbed nearly eight times less water as compared to the control specimen. Almost similar trend of water absorption was observed in 50SBT specimen.
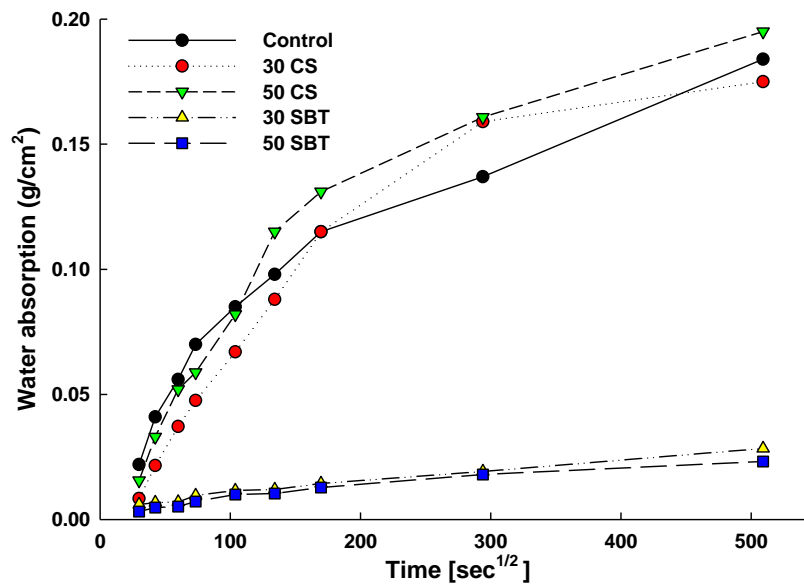

Fig. 4 Capillary water absorption of mortar specimen amended with steel slag and treated with bacteria

The reduction in the extent of water absorption may be attributed to the fact that due to bacterial calcification, $CACO_3$ crystals were deposited. This reduced the pores on the surface of the cement mortar cubes leading to protective film coating, which prevented ingress of water. The results obtained in water absorption test indicated that in 30SBT and 50 SBT specimens, the transport mechanism of water through capillary rise was altered effectively. Bacterial treatment significantly restricts the ingress of water and aggressive agents and blocks the pore with $CaCO_3$ precipitation. Similar trend of reduced water absorption in fly ash amended mortar specimen due to bio deposition was also reported (Achal et al., 2011).

Microstructural Analysis

Scanning electron micrograph and Energy dispersive X ray spectrum of 50SBT (Fig. 5A and 5B) and 30SBT (Fig. 5C and 5D) cement mortar was studied.
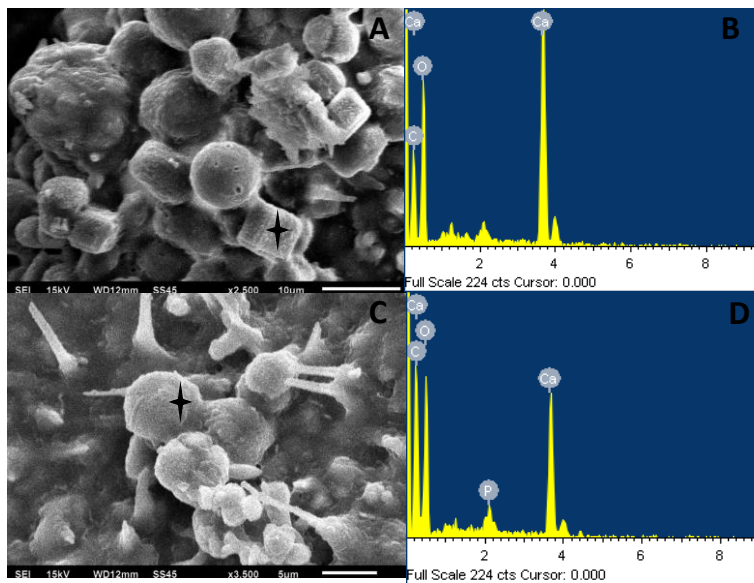

Fig. 5. Scanning electron micrograph and Energy dispersive X ray spectrum
of 50SBT (A, B) and 30SBT (C, D)

Distinct rhombohedral calcite and spheroid vaterite crystals were observed in close proximity of the bacterial cells. EDX analysis confirmed the elemental composition of crystals showing high peaks of calcium and carbon in 30SBT and 50SBT (Fig. 5B and 5D).

CONCLUSIONS

A calcifying bacterial strain with high urease activity was isolated from steel slag. Which was identified as *Staphylococcus pasteruii* based on its 16S rRNA sequence analysis. In replacement of fine aggregate with steel slag (30% and 50%) along with microbial treatment, 30SBT specimen exhibited the highest strength gain of 28% and the water ingress was reduced by eight times as compared to the control specimen. SEM analysis endorsed the involvement of bacterial cells in $CaCO_3$ precipitation. Polymorphs of calcium carbonate crystals were identified as calcite and vaterite. In conclusion, this study paved the way for sustainable production of eco-friendly building material using MICP technology and use of steel slag as an aggregate in concrete structures.

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