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A NOVEL WAY TO EXPLOIT STEEL INDUSTRY WASTE: MICROBIAL MINERALIZED SLAG BLOCKS

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Abstract

This paper presents an experimental study on the beneficial application of steel slag (SS) in the making of slag block. Steel slag and slaked lime (SL) were used in optimal proportions in the production of eco-friendly blocks. The novelty of this experiment is that bio-mineralization was induced by way of mixing certain species of bacteria in the SS-SL paste. Microbial Induced Calcite Precipitation (MICP) is a biochemical process in which bacteria precipitate calcium carbonate from a supersaturated solution. In the present study bio-blocks were developed using steel slag and employing MICP process. SS and SL were used as sources of calcium carbonate. Steel slag also served as substitute for natural sand. To induce the precipitation of calcite, bacteria species namely *Bacillus subtilis* and *Bacillus megaterium* were blended with the SS-SL mix. Under ambient curing condition and carbon dioxide pressure curing condition, SS and SL were activated in the presence of bacteria to form a stable carbonate bond matrix. Block specimens prepared with a bacterial dosage of 0.6% v/v and SL-SS in the ratio of 1:2 showed higher compressive strength as compared to that of blocks constituted with SL-SS in the ratio of 1:2.5 and blocks made without the incorporation of bacteria. SEM and XRD studies confirmed microbial activity and precipitation of calcite.

Key words: bio-mineralization, calcite precipitation, compressive strength, SEM analysis

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1. Introduction

To fulfil the essential needs of the growing population, there is rapid progress in the infrastructure development sector. The demand for construction materials is increasing and at times ends in shortage of raw materials. In this context, industrial waste products can be used as substitutes for construction materials. A large amount of industrial waste products such as steel slag and fly ash is disposed at non-engineered landfills/dump sites or farmlands or riverbanks, giving rise to environmental pollution (land-, water-, air- pollution) and health hazards. It is observed that dumping of industrial wastes on riverbanks causes silting in the riverbed. Utilization of industrial waste by-products in construction materials provides a solution for environmental pollution issues, and reduces the demand for raw materials. Moreover, low-cost construction materials could be produced from industrial waste materials (Schackow et al., 2020).

Steel is produced from the conversion of iron ore. This process is implemented in a blast furnace. Iron ore is melted along with scrap metals and flux. The molten iron is oxidized to give rise to liquid steel which is then warped into required shapes and sizes. At the end of the process molten steel slag is obtained. The molten steel slag on slow cooling transforms into solid rock-like material, and thus we get hardened steel slag as by-product from the steel manufacturing plants. In India, generation of steel slag is likely to increase enormously along with increase in the production of steel. According to Central Pollution Control Board, Ministry of Environment and Forests and Climate Change, India, about 4 million tons of steel slag is produced per annum and this huge

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quantity of steel slag is dumped at open sites. Steel slag generation is about 20% by mass of the crude steel output (IMYB, 2017). It is estimated that the production of steel slag will reach 60 million tons per annum by 2030.

Qasrawi (2014) studied the properties of concrete by using Recycled Concrete Aggregate (RCA) and Steel Slag Aggregate (SSA) and compared with that of natural aggregate. SSA concrete had 20% higher strength than that of standard concrete. Higher-strength of SSA concrete was attributed to the higher angularity of SSA that enhances the interaction between the cementitious matrix and SSA. The angular slag aggregate attributed to the radiation in the mobility of concrete. This feature resulted in reduced workability (Faleschini et al., 2016). The better bonding of the slag aggregates with hardened cement matrix and hardened inter facial transition zone contributed to the increased compressive and tensile strength of concrete (Faleschini et al., 2016; Qasrawi, 2012)

Steel slag has less potential in its application in cement clinker production; it is used as an ingredient at about 10% of the cement raw mix (IMYB, 2017). Replacement of Portland cement by steel slag (in powder form) at higher proportions in concrete mix reduces the mechanical strength of concrete. The low hydraulic property of steel slag can be attributed to the absence of amorphous silica and tricalcium silicate (Muhmood et al., 2009; Roslan et al., 2012). In the process of conversion of iron to steel, a large quantity of lime is used as flux; hence the amount of lime (CaO) is typically quite high in steel slag (Sabapathy et al., 2017; Sanjose, 2014). Among current methods of sequestering carbon dioxide (CO_2), carbonate (CO_3) mineral sequestration is considered to be a better technology since in this process the primary greenhouse gas (CO_2) is trapped permanently in the form of carbonate. Steel slag contains a large amount of CaO, and CO_2 is sequestrated in the form of calcium carbonate in steel slag (Yi et al., 2012).

Bio-calcification is the process of calcite formation in soil and structures by the action of urease enzyme-producing organisms (microbes) (Ramachandran et al., 2001). Microbial Induced Calcite Precipitation (MICP) refers to the formation of calcium carbonate from a supersaturated solution by the biochemical action of microbial cells. MICP process was applied to treat porous surface and subsurface structures (Fischer et al., 1999).

Bernardi et al. (2014) considered bacteria-induced calcite precipitation as an aid in the development of sustainable building materials and prepared sandstone bricks by compacting sand into sandstone through bacteria-induced calcite precipitation process. The strength of the sandstone bricks thus produced was comparable to that of the bricks made with other additives. Steel slag blocks were developed through the reaction of tricalcium silicate and dicalcium silicate with CO_2 in the presence of moisture. The strength development in steel slag blocks was due to the formation of $CaCO_3$ and C-S-H gel (Wang et al., 2016).

Mineralization by microorganisms gave rise to a denser and integrated structure that increased the strength of steel slag blocks. By increasing the microbes, the process of carbonation was accelerated and consequently the compressive strength of steel blocks was increased (Yi and Qian, 2018). Bio-mineralization process reduced the water absorption capacity of bricks developed with recycled aggregate to a significant level. Additionally, it improved the durability of bricks by means of maintaining the strength under freeze-thaw cycles and at high temperatures (Saeedi et al., 2018). The maximum compressive strength of microbial concrete was existed with an optimum concentration of bacteria. However it was need not to be the maximum concentration of bacteria (Ersan et al., 2015; Mondal and Ghosh, 2018).

Presently the civil engineering construction industry faces scarcity in the availability of natural coarse aggregate and fine aggregate in many instances. This difficulty could be overcome by using natural aggregate as minimum as possible and by way of substituting it with industrial waste by-product like steel slag. A positive effect on compressive strength and tensile strength was observed in concrete prepared with steel slag as fine aggregate. To produce low-strength concrete it was more advantageous to use steel slag as fine aggregate (Qasrawi et al., 2009). When steel slag was used as coarse aggregate in concrete, it increased the compressive strength of the concrete by about 7.4-7.7% above the compressive strength of concrete prepared with natural coarse aggregate, reduced the embodied energy by 4% and embodied carbon dioxide emission by 2% (Arivoli et al., 2018).

The objective of the present research is to utilize steel slag in an optimum manner and to get benefits from its CaO content efficiently in the preparation of steel slag blocks. The literature studies indicate that there is scope for research on the incorporation of steel slag in greater quantity as both binding material and fine aggregate, and under CO_2 curing in the making of steel slag bricks. This study was carried out to bring to light the binding property of steel slag (SS) and slaked lime (SL); certain species of microbes were incorporated as catalyst in the SS-SL mix. The biochemical reaction involved hydration of carbon dioxide to precipitate more carbonates in steel slag blocks.

2. Experimental program

2.1. Materials

2.1.1. Steel Slag

M/s JSW Steel Limited, Salem Works (JSWS), Tamil Nadu, India generates steel slag (SS) to the tune of about 12,000,000 m^3-30,000,000 m^3 per annum. From this plant SS was obtained. Raw and aged SS particles were collected from the JSWS yard and graded through sieve analysis. SS particles conforming to the size of fine aggregate as per specifications (IS 383, 1973 and ASTM C136, 2019) were collected from the sieve and utilized in this study. One kg of oven dried steel slag was sieved through the standard sieves of 4.75 mm, 2.63mm, 1.18 mm, 600 µ, 300 µ and 150 µ. The residues on the each sieve were weighed and cumulative percentages retained on the each of the sieve were calculated. The sum of the cumulative percentage divided by 100 gives the fineness modulus of steel slag as 3.1. The density and water absorption of SS fine aggregate was determined through standard tests (ASTM C128, 2015) and found to be 3020 kg/m^3 and 1% respectively.

The SS fraction that passed through 4.75 mm sieve was collected as SS powder. It was used as binder in the bio-block mix. The specific surface area of SS powder was determined and it was found to be 320 m^2/kg. This value conformed to the specifications for SS powder prescribed by IS 4031 Part 2. The chemical composition of SS powder is presented in Table 1. The primary chemical oxides identified were CaO, MgO, SiO_2, and Al_2O_3 (Brand and Roesler, 2015; Rojas and Rojas, 2004; Sanjose, 2014).

In the process of conversion of molten pig iron into steel, a certain percentage of iron is captured as hot metal, and this fraction cannot be streamlined into the production of steel. This oxidized iron is observed in the chemical analysis steel slag specimen. Owing to the fact that a large amount of lime (CaO) is used as flux in the conversion process of iron into steel, the CaO content in steel slag is typically very high (Sabapathy et al., 2017; Sanjose, 2014).

The mineralogical composition of SS was determined through X-ray diffraction (XRD) studies. The diffraction pattern of SS is illustrated in Fig. 1. It shows the presence of minerals namely, lanite – Ca_2SiO_2 (L), hematite – (H), calcite – $CaCO_3$ (C), gehlenite – Ca_2Al ($AlSiO_7$) (G), and wustite – FeO (W). Owing to its high crystalline nature, SS has limited potential for application in any hydraulic activity conforming to dimensional stability. Energy optimized furnace (EOF) steel slag does not have any pozzolanic property due to its high degree of crystalline state (Rojas and Rojas, 2004). The high degree of crystallinity of SS significantly contributes to the volume stability of SS, which is one of the major requirements for a sound aggregate used in concrete (Monsosi et al., 2006; Pellegrino and Gaddo, 2009).

2.1.2. Slaked lime

Slaked lime - calcium hydroxide – $Ca(OH)_2$ is an inorganic compound. It is available in the form of colourless crystals or white powder. Quicklime is produced from burning of limestone.

Slaked lime is obtained by mixing quicklime (CaO) with water. Slaked lime was used in this study to activate the hydration of steel slag that can help to improve the early mechanical characteristics of blocks (Wang et al., 2016, 2021). Chemical composition of steel slag (SS) powder and slaked lime (SL) determined by x-ray fluorescence spectrometry, is presented in Table 1.

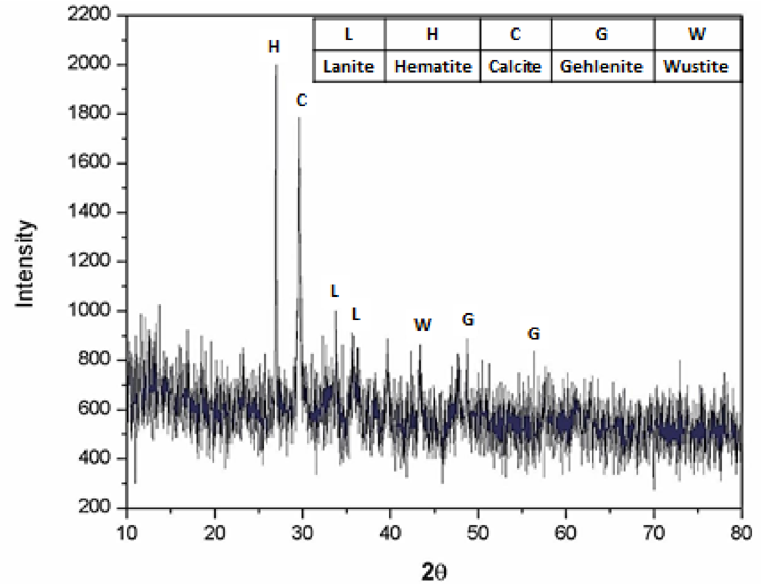

Fig. 1. X-ray diffraction analysis of SS

Table 1. Chemical composition of steel slag (SS) powder and slaked lime (SL)

Oxide Composition (Wt. %)	*CaO*	*MgO*	*SiO_2*	*Al_2O_3*	*MnO*	*FeO*	*P_2O_5*	*Na_2O*	*K_2O*	*SO_3*
SS powder	35.28	9.27	16.69	6.20	1.88	26.91	1.43	0.16	0.03	0.56
SL	99.80	-	-	-	-	-	-	-	-	-

2.1.3. Calcium carbonate precipitating bacteria

In the present study, cultures of bacteria species namely, *Bacillus megaterium* (*B. megaterium*) and *Bacillus subtilis* (*B. subtilis*) were used as catalyst to induce carbonation. *Bacillus megaterium* is commonly known as soil bacterium. It is a spore-forming aerobic bacterium and is found in distinct environments. It can feed on various carbon sources and grow in a wide range of temperature from 3^0C to 45^0C (Saeedi et al., 2018). These characteristics of B. *megaterium* make it ideal for industrial applications. *Bacillus subtilis* is also aerobic spore-forming bacterium, and is commonly found in vegetation and soil. Typically, *B. subtilis* can evolve under difficult environmental conditions, and thus it becomes most suitable for industrial usage (Boominadhan et al., 2009). The bacterial concentrations of 10^7-10^9 cfu/ml have considered for crack healing in cementitious concrete and it is obvious that higher concentration of bacteria enables higher calcium carbonate precipitation. As the steel slag has less pozzolanic property, a higher concentration of bacteria (10^9cfu/ml) was adopted in this study (Ersan et al., 2015). Cultured bacteria (*B. megaterium* and *B. subtilis*), having the following specifications were procured from M/s TRM Bio-Tech Company: bacteria potency = 2 x 10^9 cfu/ml; bacterium content = 30-40% in 500 ml; enzymes and vitamins = 5% in 500 ml; and non-pathogenic.

2.1.4. Preparation of specimens

Twelve mix proportions were prepared by varying the ratio of slaked lime to steel slag, bacteria species, and curing condition. Two ratios of slaked lime to steel slag, 0.4 and 0.5, were adopted. Two kinds of bacterium namely, *Bacillus megaterium* and *Bacillus subtilis* were used. SL-SS mix was the binder. Water to binder ratio and SS fine aggregate to binder ratio were kept as 0.6 and 2 respectively. The mix kinds were designated alphanumerically. Letters were used to represent the kind of bacterium used in the mix and the curing condition - the letters M and S for *Bacillus megaterium* and *Bacillus subtilis* respectively, and the letters S and C for standard/normal curing and carbonation curing respectively. Binder ratios of 0.4 and 0.5 were indicated correspondingly as B4 and B5. Thus, a block specimen made from mix prepared with slaked lime to steel slag ratio of 0.4 and *Bacillus megaterium*, and under carbonation curing condition was named as B4-M-C. Control block specimens without the incorporation of bacteria were also prepared. The names (codes) of the mix proportions and related details are presented in Table 2.

All the mix proportions were formulated with a regular water content of 315 L/m^3. Bacteria culture was prepared in the concentration of 50 L/m^3. Moulds of size 230 mm x 110 mm x 75 mm were fabricated to cast the blocks. Raw materials of the mix proportions were blended uniformly to get a consistent mix. The prepared mixes were poured into moulds. After 24 hours, the block specimens were taken out from the moulds and covered with polythene sheets to prevent moisture loss. All the polythene sheet-wrapped block specimens were kept at 30^0C for 24 hours.

The block specimens assigned for standard curing were cured under normal conditions at 30^0C and relative humidity of 66%. Additionally, air was supplied adequately for 15 days to bring about bio-mineralization by aerobic bacteria (*B. megaterium* and *B. subtilis*) and to ensure availability of oxygen for the transformation of CO_2 to carbonate.

The block specimens that were meant for carbonation curing were cured in a specially designed chamber. A schematic diagram of carbonation curing appears in Fig. 2. The setup consisted of a cylinder filled with 99% pure CO_2, a pressure regulator to control pressure in the carbonation chamber, and a pressure transducer to monitor the gas pressure. The block specimens were placed in the carbonation chamber and were cured with the application of CO_2 at a pressure of 0.3 MPa for 3 hours and then were kept in rest for 15 days at 30^0C and relative humidity of 66%.

Table 2. Mix proportions for blocks

Mix	*SL/SS*	*SS*		*SL (kg/m³)*	*Bacteria type*	*Curing*
		As binding powder (kg/m³)	*As fine aggregate (kg/m³)*			
B4-S	0.4	450	1260	180	-	Standard
B4-C	0.4	450	1260	180	-	Carbonation
B4-M-S	0.4	450	1260	180	*B. megaterium*	Standard
B4-M-C	0.4	450	1260	180	*B. megaterium*	Carbonation
B4-S-S	0.4	450	1260	180	*B. subtilis*	Standard
B4-S-C	0.4	450	1260	180	*B. subtilis*	Carbonation
B5-S	0.5	420	1260	210	-	Standard
B5-C	0.5	420	1260	210	-	Carbonation
B5-M-S	0.5	420	1260	210	*B. megaterium*	Standard
B5-M-C	0.5	420	1260	210	*B. megaterium*	Carbonation
B5-S-S	0.5	420	1260	210	*B. subtilis*	Standard
B5-S-C	0.5	420	1260	210	*B. subtilis*	Carbonation

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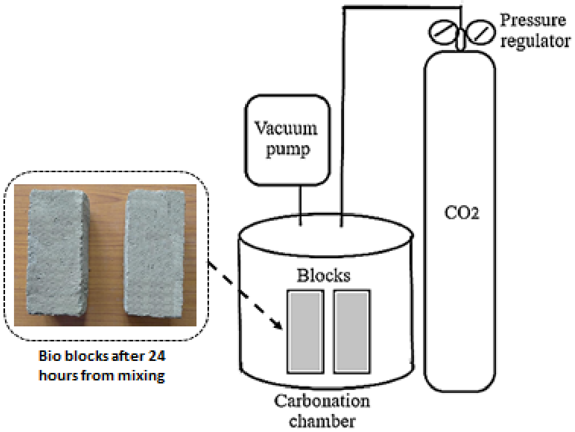


Fig. 2. Schematic representation for mineralization

3. Experimental investigation

The block specimens were tested for their compressive strength and water absorption capacity following the prescribed guidelines (IS 3495, 1992a, 1992b and ASTM C67, 2020). In carrying out compressive strength test, the specimens were placed with their horizontal faces lying horizontally between two sheets of 3-mm thick plywood. This arrangement ensured uniform distribution of applied load. Load was applied at a rate of 14 N/mm^2 per minute. The load at which failure occurred was taken as maximum load. Average of six readings of maximum load corresponding to six specimens was calculated.

For conducting the water absorption capacity test, six block specimens were taken and dried to constant mass in an oven at a temperature of 105^0C to 115^0C. After drying and cooling at room temperature, the block specimens were weighed to a precision of 1 g and then were immersed fully in water for 24 hours. After 24 hours, the specimens were taken out and wiped cleanly using a cloth to remove surface water and were weighed to know their wet mass (Kizinievic et al., 2020).

The precipitation of calcium carbonate can be perceived by the amount of CO_2 uptake by the block specimens. Mass change in blocks before and after carbonation was observed to measure the CO_2 uptake. The mass of the block specimen before carbonation was weighed as m_0. The binder mass (m_b) was calculated as shown in Eq. (1) because of the ratio of binder: fine aggregate: water was *x: y: 0.6x*. The mass of the dry blocks (m_1) without water can be calculated as shown in Eq. (2). The mineralized slag blocks were dried to constant mass in an oven at a temperature of 105^0C to 115^0C and the mass of the block was noted as m_2. The measure of CO_2 precipitated as $CaCO_3$ by the blocks was $m_2 - m_1$. Hence the CO_2 absorption ability of binder (C_b) can be calculated as in Eq. (3).

$$m_b = \frac{m_0 x}{1.6x + y} \tag{1}$$

$$m_1 = m_0 - 0.6\ m_b \tag{2}$$

$$C_b = \frac{m_2 - m_1}{m_b} x100 \tag{3}$$

where: *x*, *y* is the ratio of slag blocks; m_0 is the mass of the block specimen before carbonation; m_b is the mass of steel slag and slaked lime in blocks; m_1 and m_2 were mass of blocks before and after carbonation without water; and C_b is the CO_2 absorption ability of binder.

XRD and SEM studies were carried out on the block specimens to understand the mechanism of microbes-induced calcite precipitation and to discern the micro structure of calcite precipitate and its mineralogical composition.

4. Results and discussion

4.1. Compressive strength of block specimens

Fig. 3 and Fig. 4 illustrate the strength development of block specimens prepared under standard curing condition and carbonation curing condition respectively. Irrespective of the kind of bacteria species (*B. megaterium* or *B. subtilis*) incorporated in the mix, block specimens prepared from using mix proportions with SL-SS ratios of 0.4 and 0.5 and cured under carbonation condition show higher strength gain than block specimens prepared under standard curing condition. Among the block specimens cured under standard curing conditions, the strength gain of block specimens B4-M-S and B5-S-S is 4 times and 5 times the strength of block specimens prepared from mix proportion without the incorporation of bacteria (B4-S). The same trend is observed in respect of block specimens B5-M-S and B5-S-S whose strength gain is 3 times and 3.5 times respectively the strength of block specimens prepared from mix proportion without the incorporation of bacteria (B5-S). The precipitation of calcium carbonate depends on the concentrations of calcium and dissolved carbon and the availability of bacteria as a nucleation site (Dhami et al., 2013). The active role of bacteria can be understood from the strength gain attained by block specimens prepared from mix with bacteria over block specimens prepared from mix without bacteria. The precipitated calcium carbonate crystals bind the particles strongly and improve the overall integrity of the block specimens.

From Fig. 3 and Fig. 4, it is gathered that the block specimens prepared from mix containing bacteria and treated under carbonation curing show improved strength over the block specimens lacking in nucleation sites. The compressive strength of block specimens B4-M-C and B4-S-C is improved by 100% and 150% respectively as compared to the compressive strength of block specimen B4-C. Similarly, the block specimens B5-M-C and B5-S-C show improvements in compressive strength to the tune of 80% and 110% respectively as compared to the compressive strength of block specimen B5-C. The improvement in compressive strength of bio-block specimens is explained as follows.

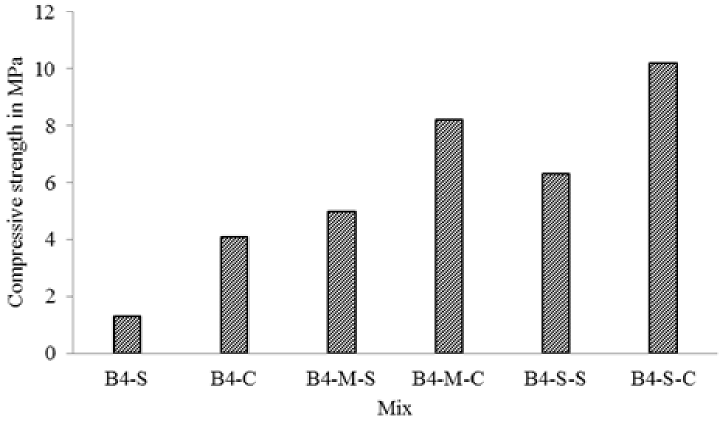


Fig. 3. Compressive strength of blocks with SL/SS as 0.4

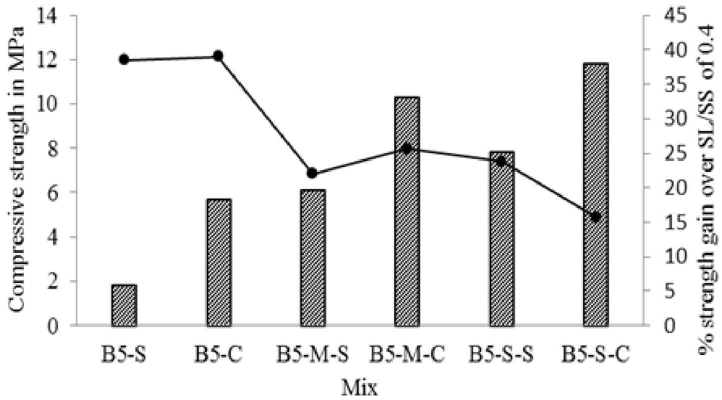


Fig. 4. Compressive strength of blocks with SL/SS as 0.5

With an increase in the concentration of CO_2 and at a pressure of 0.3 MPa, precipitation of calcium carbonate was greatly induced by bacteria; furthermore, owing to the high amount of calcium present in steel slag and slaked lime, the bacteria consumed more calcium and precipitated it in the form of calcium carbonate (Yi and Qian, 2018).

Considering the mixes prepared with SL/SS as 0.4 and 0.5, the bacterium *Bacillus subtilis* sustained its adaptability with steel slag better than the bacterium *Bacillus megaterium*; hence the compressive strength B4-S-C and B5-S-C is 25% and 15% higher than the compressive strength of B4-M-C and B5-M-C respectively.

The compressive strength of block specimens prepared from mix having SL/SS = 0.5 and their strength gain expressed in percent over block specimens prepared from mix having SL/SS = 0.4 are portrayed as bar chart and graph respectively in Fig. 4. The strength gain in respect of block specimens B5-S (standard curing) and B5-C (carbonation curing) is around 40%, whereas it is in the range of 16% to 26% in respect of block specimens prepared with bacteria.
Though the concentration of carbon and the nucleation sites are uniform for both ratios of SL/SS, the strength gain in B5-group of block specimens is due to the availability of concentrated calcium. The variation in calcium concentration is reflected in the rate and amount of calcium carbonate formation. Negatively charged bacteria reacted with free Ca^{2+} ions and promoted the formation of calcium carbonate (Dhami et al., 2013; Yi and Qian, 2018).

4.2. Water absorption capacity

Fig. 5 and Fig. 6 show the water absorption capacity of block specimens prepared from mixing having two different SL/SS ratios 0.4 and 0.5. Owing to the formation of more number of $CaCO_3$ crystals and to the availability of CO_2 in high concentration, the water absorption capacity of the block specimens treated with carbonation curing is less than that of the block specimens cured under standard conditions. The $CaCO_3$ crystals strongly bind the steel slag fine aggregate together.

Considering the SL/SS ratios (0.4 and 0.5), kind of bacteria species (*Bacillus megaterium* and *Bacillus subtilis*) and curing conditions (standard curing and carbonation curing), it is found that prepared with SL/SS = 0.4, the block specimens B4-M-C and B4-S-C show 19% and 7% less water absorption than B4-M-S and B4-S-S respectively, whereas produced with SL/SS = 0.5, the block specimens B5-M-C and B5-S-C show 12% and 7% less water absorption than B5-M-S and B5-S-S respectively.

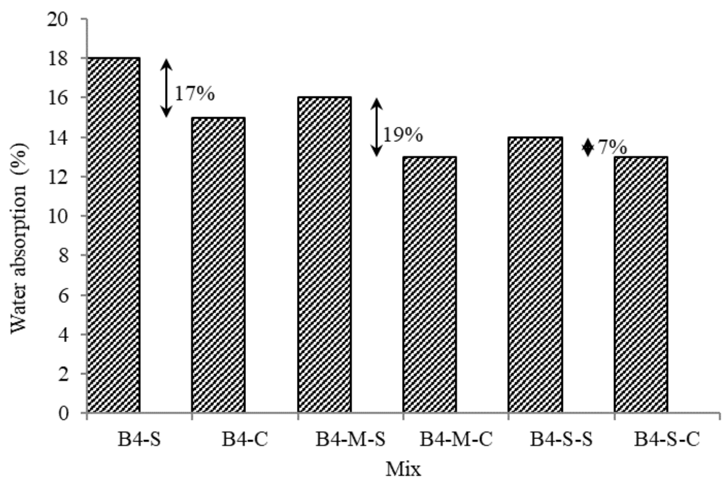


Fig. 5. Water absorption of blocks with SL/SS as 0.4

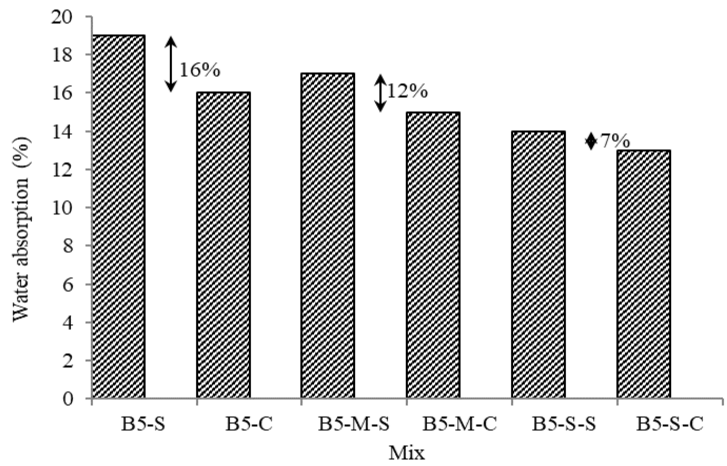


Fig. 6. Water absorption of blocks with SL/SS as 0.5

Water absorption capacity of block specimens prepared with the incorporation of bacteria and under carbonation curing, viz., B4-M-C, B4-S-C, B5-M-C, and B5-S-C is less than that of block specimens namely, B4-C and B5-C made without the addition of bacteria but cured under carbonation. The degree of calcium carbonate precipitation is high in block specimens imbued with bacteria; the calcium carbonate precipitate fills the pores in the block specimens and very well binds the steel slag particles together (Kucharski et al., 2006; Sarda et al., 2009). In respect of block specimens of both SL/SS ratios (0.4 and 0.5), the block specimens containing *B. subtilis* possess low water absorption as compared to that of block specimens containing *B. megaterium*. Another observation is that calcium ion concentration is one of the factors that influence the precipitation of calcium carbonate; the B5 group block specimens have higher calcium content and hence their water absorption is less than that of B4 group block specimens.

4.3. CO_2 uptake of blocks

In mineralisation, the diffused CO_2 got hydroxylated with water and produced CO_3^{2+}. Thus produced CO_3^{2+} collide with Ca^{2+} and will deposit $CaCO_3$ in the pores of steel slag blocks (Wang et al., 2016). The CO_2 uptake of the mixes prepared with SL/SS as 0.4 and 0.5 is given Fig. 7. It can be perceived that B5-M-C and B5-S-C exhibited higher carbon uptake for per unit mass of binders such as steel slag and slaked lime which reached 7.56% and 8.27% at 15 days, respectively. Where in B4-group of block specimens, B4-M-C and B4-S-C presented 6.76% and 7.73% of carbon uptake per unit mass of binders. This was related to higher relative mass ratio of slaked lime and steel slag in B5- group than that of B4- group. The availability of free Ca^{2+} is low when the slaked lime content is low. The chance of Ca^{2+} and CO_3^{2+} collision increased which in terms increased the $CaCO_3$ deposition, thus the strength of block specimen increased.

The mineralisation and crystal growth of $CaCO_3$ covers on the surface of slag and lime particles. As the mineralisation proceeds, the mineralized products accumulate continuously. The calcium carbonate formed on the surface of slag and lime particles begins to contact with each other and binds the aggregate together heading to dense structure and contribution of compressive strength.

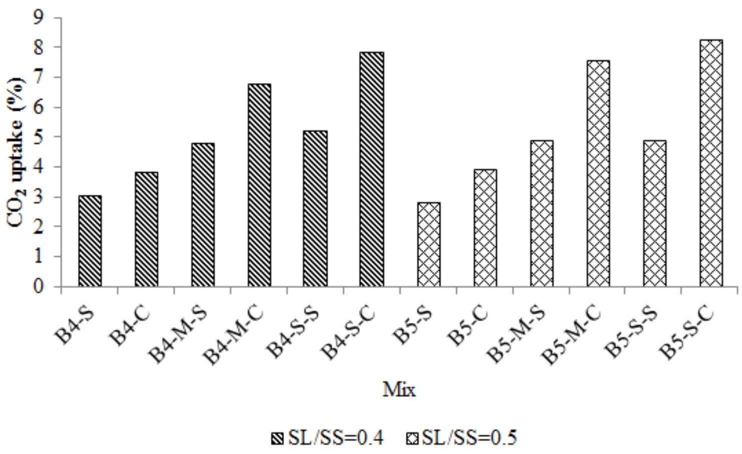


Fig. 7. Carbon uptake of blocks with various SL/SS ratio

4.4. Mechanism of microbial induced calcite precipitation

Microbial induced calcite precipitation in steel slag and lime mix is graphically presented in Fig. 8. Bacterial surfaces play a crucial role in mineralization. During the process of mineralization in SS-SL mix, positively charged calcium (Ca^{2+}) ions bind with the negatively charged bacterial surface. This bacterial surface acts as the nucleation site for the precipitation of calcium carbonate (Fortin et al., 1997). Calcium required for the growth of the bacteria is supplemented from the free calcium ion stock of the steel slag-slaked lime mix. Bacteria release ammonia and carbonic acid through intracellular hydrolysis. These products equilibrate in water and form bicarbonate (HCO_3) ions. The bicarbonate ions react with the free calcium ions and form calcium carbonate. Calcium carbonate precipitation progresses on the external surface of bacteria by continuous stratification. Thus bacteria can be embedded in SL-SS mix to accumulate calcium carbonate crystals (Rivadeneyra et al., 1998).

4.5. Analysis of microstructure of calcite precipitate

Increase in the strength of steel slag block specimens prepared from mixes incorporated with bacteria could be attributed to microbial induced calcite precipitation. Block specimens prepared with and without bacteria were examined under scanning electron microscope (SEM). SEM micrograph of specimens prepared without bacteria under standard curing and carbonation curing are presented in Fig. 9a and Fig. 9b respectively. SEM image of specimen cured under standard condition shows platy rough edged structures with less calcium carbonate precipitation and the specimen cured under carbonation shows calcite crystal deposition on steel slag that was not significant enough to bind the steel slag aggregate together. SEM micrograph of a block specimen prepared with the incorporation of bacteria and under standard curing condition appears in Fig. 9c. It shows clearly the accumulation of bacteria in considerable counts on the surfaces of steel slag fine aggregate. Fig. 9d shows the micrograph of a block specimen prepared with the addition of bacteria and under carbonation curing. In this micrograph, a denser deposition of calcite can be seen on the surface of the steel slag fine aggregate. Calcite crystals are well compacted and tightly formed. Sharp edges of the calcite crystals are distinct indicating the wholesome development of the crystals. The calcite crystals strongly bind the steel slag aggregate together and thus give rise to a highly dense structure. The surface of calcite deposition has many boundaries and textures. This rough surface also contributes to the strength gain in blocks. This improvement in strength is an additional advantage got from bacteria induced mineralization.

4.6. Mineralogical composition

XRD patterns of normally cured and CO_2 cured block specimens prepared from mixes with the incorporation of bacteria are shown in Fig. 10a and Fig. 10b respectively. Carbon dioxide (CO_2) stimulates the transformation of C_2S and $Ca(OH)_2$ into calcium carbonate. The significant distinction between the XRD patterns of block specimens prepared with the incorporation of bacteria and treated under standard curing and carbonation curing is the intensity of calcium carbonate. Since the amount of microbially precipitated calcium carbonate is higher in CO_2 cured block specimen than in normally cured block specimen, the intensity peak of $CaCO_3$ of carbonation cured, bacteria incorporated block specimen is higher than that of normally cured, bacteria incorporated block specimen. The high peaks of calcium diffraction also indicate the good crystallization quality of calcium carbonate and magnesium carbonate (Hou et al., 2020; Wang et al., 2016).

Owing to the microbial deposition of more amount of calcium carbonate in carbonation cured block specimens, the compressive strength of microbially mineralized, carbonation cured block specimens is higher than that of microbially mineralized, normally cured block specimens.

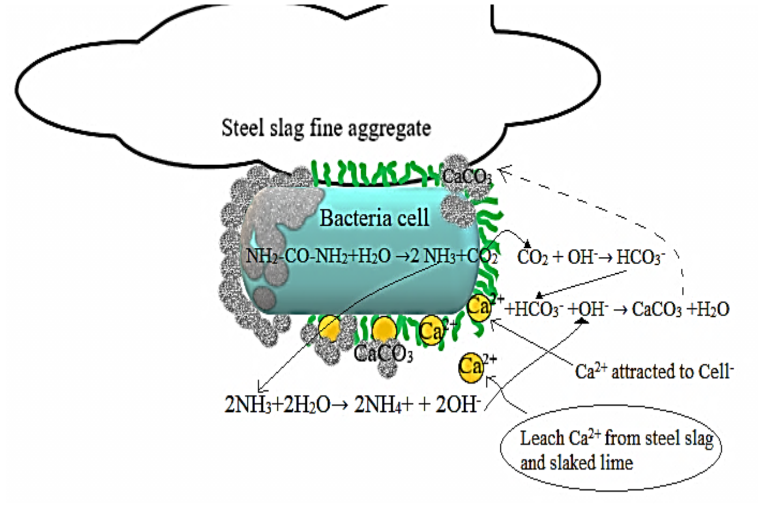


Fig. 8. Bacteria favoring as nucleation site for $CaCO_3$ precipitation on steel slag fine aggregate

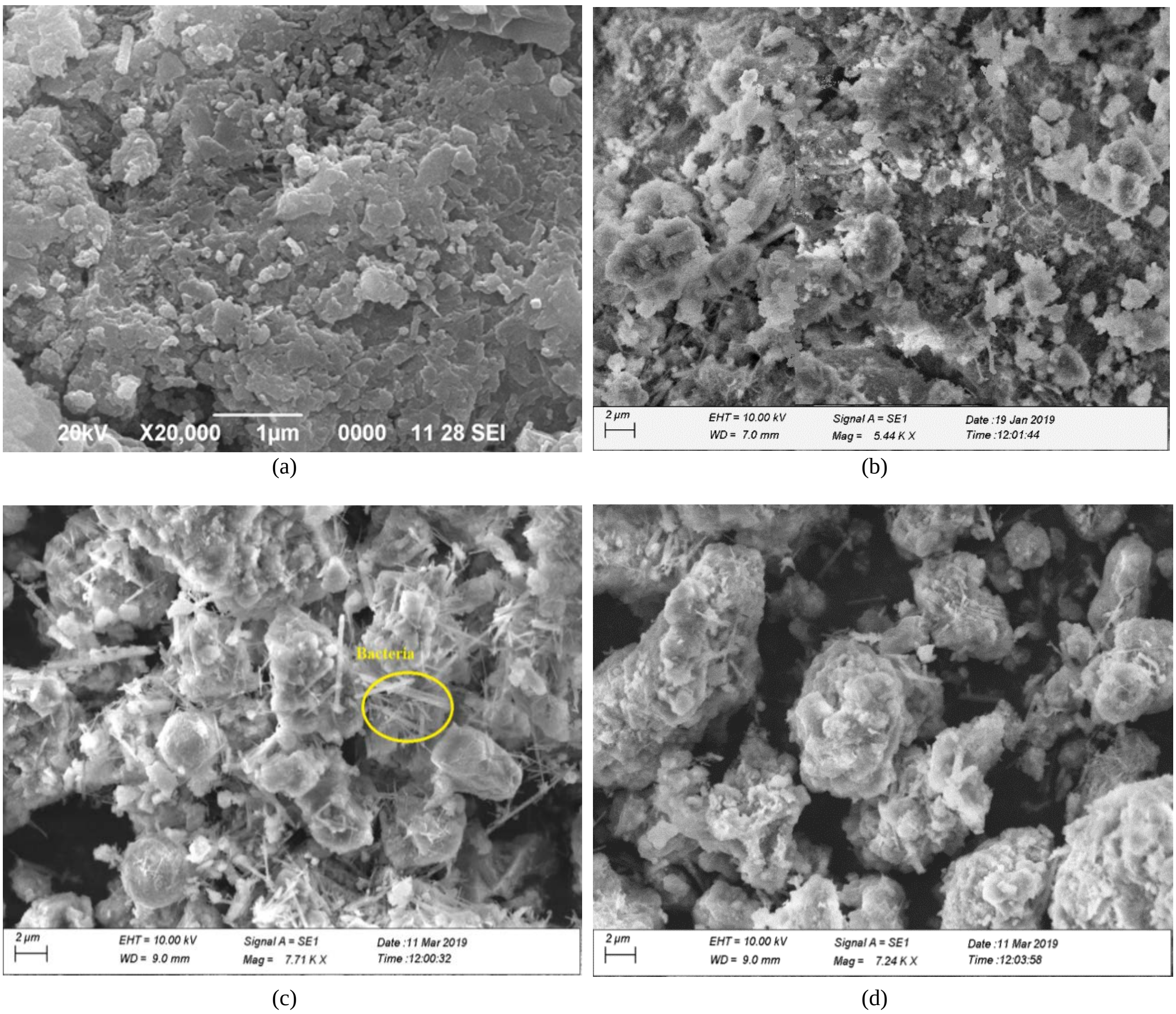
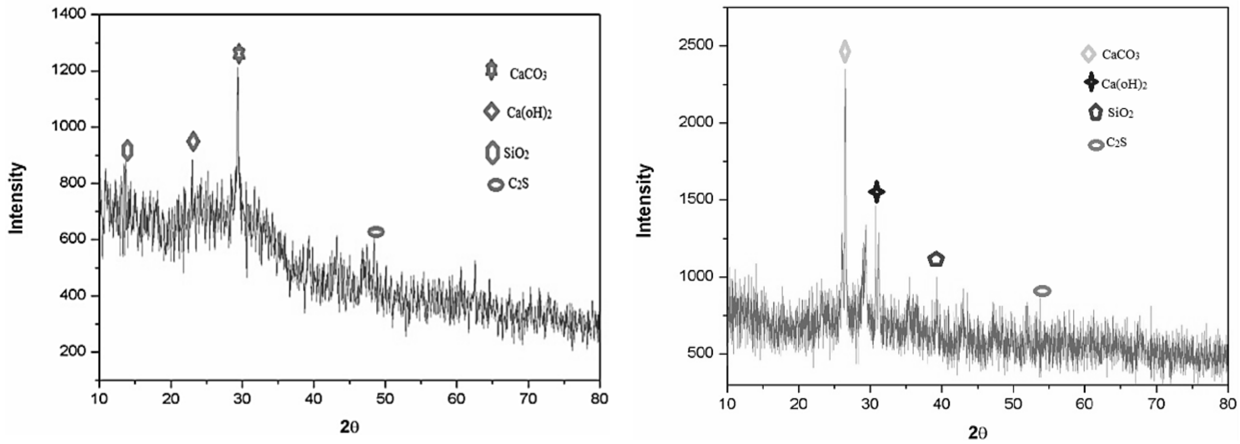


Fig. 9. (a) SEM image of sample without bacteria cured under standard condition, (b) SEM image of sample without bacteria cured under carbonation condition, (c) SEM image of bacteria inducing mineralization on steel slag, (d) SEM image of calcite precipitation



(a) (b)

Fig. 10. (a) XRD pattern of normally cured bio-block specimen, (b) XRD pattern of carbonation cured bio-block specimen

5. Conclusions

From the experimental investigations, it is found that steel slag block specimens prepared from mix with SL/SS = 0.5 and infused with *Bacillus subtilis* show highest compressive strength of 12 MPa. Higher concentration of calcium contributes to precipitation of highly dense calcium carbonate. The bacteria species *Bacillus subtilis* serve as most adaptable nucleation sites for microbes induced precipitation.

Calcium carbonate crystals develop on the external surface of bacteria. The steel slag particles are strongly bound together by calcium carbonate precipitate and thus the overall integrity of the block specimens is improved. Calcium carbonate crystals fill the pores in the blocks, and the water absorption of the blocks is considerably reduced. The SEM images confirm the formation of solid calcium carbonate crystals with an irregular surface and rough texture. These aspects contribute to the strength gain in steel slag blocks. XRD patterns of block specimens prepared with the incorporation of bacteria and cured with CO_2 show a sharp increase in the diffraction peak of calcium, indicating the good quality of calcium carbonate crystals formed from microbes induced precipitation.

The microbes accelerate the carbonation of steel slag and slaked lime in the mineralization process. Bacteria bring about the precipitation of $CaCO_3$ with the dissolution of Ca^{2+} present in the steel slag and slaked lime. Calcium silicate present in the steel slag and $Ca(OH)_2$ are mineralized to form $CaCO_3$ crystals. Mineralization closes the pores in the blocks and the strength of the blocks is increased.

Considering the merits of steel slag as explained in this paper, steel slag, along with the incorporation of non-pathogenic bacteria in the mix could be very well used in the making of bio blocks. Steel slag serves in a dual way in slag blocks both as binder and fine aggregate. The bio blocks thus prepared could function as an ideal storage stock for the sequestration of CO_2. Microbes incorporated steel slag blocks (bio blocks) could be considered as environment-friendly, sustainable building materials.

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