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# The properties and mechanism of microbial mineralized steel slag bricks

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## HIGHLIGHTS

- Preparation of microbial mineralized steel slag bricks is at room temperature, gas pressure is just 0.3 MPa, no molding pressure.
- Calcium carbonate is the gelled product through microbial mineralization.
- Utilize the industrial waste steel slag and absorb the industrial carbon dioxide.

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## ABSTRACT

An experimental program was carried out to investigate the possibility of producing microbial mineralized steel slag bricks through mineralization. The properties of different steel slag bricks such as strength and carbon uptake were mainly investigated. Mineralization could significantly improve the strength, the optimal SL/SS ratio for the microbial mineralized steel slag bricks is 0.3. Through 3-h mineralization after demoulded, the highest compressive strength of the steel slag bricks can up to 17.1 MPa, flexural strength up to 4.22 MPa. Through X-ray diffraction (XRD), mercury-intrusion porosimetry (MIP), scanning electron microscopy (SEM), and differential thermal and thermogravimetric analysis (DTA/TG), the mechanism of the microbial mineralized steel slag bricks was analyzed and discussed.



## 1. Introduction

Steel slag is a major by-product of the steel refinery process [1]. And the amount of it is generally 12–20% of crude steel production [2]. Chinese steel production is expected to reach 8.14 million tons, with an annual output of more than 120 million tons of steel slag, and it is predicted that the steel slag would remain rapid growth within more than 3000 tons per year in the future. However, the current utilization rate of steel slag in china is only 22%, far behind the developed countries like USA, Japan, German and France, of which the rates have been close to 100% [3]. At present, the amount of slag deposited in storage yard adds up to 30 Mt, leading to the occupation of farm land and serious pollution to the environment. In comparison to ground granulated blast-furnace (GGBF) slag, steel slag is much weaker in cementitious behavior [4]. The main difference between the two types of slag is that GGBF slag is amorphous due to fast cooling while the structure of steel slag is crystalline, formed in a slow cooling process.

Although steel slag is latently hydraulic, it can be activated by carbon dioxide ($CO_2$) to form a strength-contributing, carbonate-bond matrix. The tricalcium silicates ($3CaO{\cdot}SiO_2$ or $C_3S$) and dicalcium silicates ($2CaO{\cdot}SiO_2$ or $C_2S$) in slag react with $CO_2$, promoting a rapid strength gain through the formation of calciumsilicate-hydrates ($3CaO{\cdot}2SiO_2{\cdot}3H_2O$ or C-S-H) and carbonates ($CaCO_3$) [1]. The principal reactions are given in Eqs. (1) and (2) [5].

$$2(3CaO \cdot SiO_2) + 3CO_2 + 3H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3CaCO_3 \quad (1)$$

$$2(2CaO \cdot SiO_2) + CO_2 + 3H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + CaCO_3 \quad (2)$$

Studies of carbon reactivity of steel slag for product development are scarce. Porous slag blocks (1 $m^3$) were produced by carbonation of steelmaking slag over a period of 12 days. The compressive strength and bulk density of the blocks were 18.4 ± 3.3 MPa and 2.4 $g/cm^3$, respectively [6]. Unconfined compressive strengths of 9 MPa were recorded in carbonated compacts on exposure to carbon dioxide ($CO_2$) at a pressure of 3 bars, compacts formed from pressed ground slag [7]. Electric arc furnace

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(EAF) slag can also be activated by carbon dioxide to achieve a strength of 17 MPa and a carbon uptake of 11% in 2-h carbonation [8]. When the SL/SS ratio is 0.2, the carbonated steel slag-slaked lime mixture sample possesses compressive strength of 22.7 MPa and flexural strength of 5.3 MPa, respectively [9].

Steel slag are regarded as the ideal feedstocks for $CO_2$ sequestration [10]. However, the $CO_2$-sequestration efficiency is not very high. Therefore, the study of improving the $CO_2$-sequestration efficiency is very important. The use of microbially induced carbonates as a binder material, i.e. biocementation, is reported [11]. Microbes and their enzymes play an important role in the natural environment. Given a necessary reaction time, microbes help to coagulate the incompact sand and stones into hard and large-sized rocks. These rocks are mostly calcite-based materials [12]. The microbes that are important in this process are called carbonate-mineralizing bacteria [13]. Microbes are indispensible for the calcite precipitation system. This particular mineralization process is labeled as Microbial Calcite Precipitation, the chemical reactions are given in Eqs. (3) [12].

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \tag{3}$$

According to Cao and Yang's research [14], this paper will use carbonate-mineralizing bacteria to improve the $CO_2$-sequestration efficiency of carbonated steel slag-slaked lime (SS-SL) mixture. Slaked lime can activate the steel slag [15], and moreover, it will provide a source of calcium for Microbial Calcite Precipitation. Therefore, in order to simplify the manufacturing process and recycle $CO_2$ in tail gas directly, this study used steel slag, slaked lime and carbonate-mineralizing bacteria to prepare a new building material—microbial mineralized steel slag brick. Before application of microbial mineralized steel slag brick, further investigation is needed. Hence, in this paper, mainly the properties of the microbial mineralized steel slag brick and its mechanism were investigated.

## 2. Experiment

### 2.1. Raw material

Steel slag with a specific area of 450 $m^2$/kg and density of 3170 kg/$m^3$ powder from Shanghai Baoye Slag Comprehensive Development Co. Ltd. Calcium hydroxide AR (slaked lime) from Shanghai LingFeng chemical agent Ltd. The chemical compositions of steel slag and calcium hydroxide by X-ray fluorescence spectrometry (XRF) are summarized in Table 1.

The particle size of the steel slag was smaller than 200 μm with the color of gray. And the content of CaO in steel slag powder was 43.7%, which was a great potential in use. In order to stimulate the potential in steel slag, a certain amount of calcium hydroxide was used.

Fig. 1 shows SEM photomicrographs of the steel slag powder, the fine granular steel slag powder is more porous and coarser. Active mineral were not discernible in the steel slag at this magnification, but were clearly visible as stacked.

As shown in the XRD pattern of steel slag in Fig. 2, steel slag contains some $C_2S$, but due to the lack of $C_3S$ and the presence of large amount of iron oxides (FeO, $Fe_3O_4$), which has no cementitious properties [4], its hydraulic activity is rather low. Furthermore, steel slag also contains some f-CaO, which could result in the uncontrolled volume expansion [16].

River sand with a modulus of 2.28 and bulk density of 1470 kg/$m^3$ were used as aggregate. Additionally, $CO_2$ with about 20% concentration produced from Nanjing Shangyuan industrial gas plant was used to create a carbonation environment, similar to that in tail gas.

The *Bacillus mucilaginous* powder was purchased from the China Center of Industrial Culture Collection (CCIC).

**Table 1**
Chemical composition/w%.

| | CaO | $SiO_2$ | $Al_2O_3$ | MgO | $Fe_2O_3$ | $P_2O_5$ | $SO_3$ |
|---|---|---|---|---|---|---|---|
| Steel slag | 43.7 | 13.1 | 5.1 | 0.0 | 27 | 7.2 | 0.6 |
| Slaked lime | 99.9 | – | – | – | – | – | – |

### 2.2. Sample preparation

Twenty mix proportions by varying the SL/SS ratio (by dry weight), amount of bacterial powder, mineralization time are given in Table 2. Their water/binder (SS + SL) ratio and sand/binder ratio are fixed at 0.5 and 2.0, respectively. Group A is un-mineralized steel slag brick, Group B is mineralized steel slag brick, Group C is microbial un-mineralized steel slag brick, Group D is microbial mineralized steel slag brick.

The raw materials were mixed with water for 4 min first, and then were cast into molds of 40 mm × 40 mm × 160 mm. All samples were demoulded after 24 h curing at 60% ± 5%RH and 25 ± 2 °C. Then half of the samples (Group B and Group D) were mineralized completely in the carbonation equipment with the $CO_2$ concentration of 20% ± 1%, the gas pressure was 0.30 MPa, the mineralization time was 3 h, 60% ± 1%RH and 20 ± 1 °C to prepare the mineralized brick. The other half (Group A and Group C) was placed in the sealed chamber with 20 ± 1 °C and 60% ± 1%RH for the same duration to prepare the un-mineralized bricks, as references.

A schematic representation of the mineralization setup is shown in Fig. 3. It consists of a compressed $CO_2$ gas cylinder with 20% purity, a carbonation chamber, a pressure transducer and a pressure regulator. The pressure transducer monitors gas pressure and the regulator maintains the chamber pressure at a constant of 0.3 MPa throughout the mineralization process.

In order to further investigate the mechanism of the mineralized brick, paste samples were used for the sake of eliminating the aggregate effect. The paste samples were prepared through the same procedure, and their mix proportions are listed in Table 2, but without aggregates.

### 2.3. Test methods

According to the Chinese test methods for wall bricks (GBT2542-2003) [17], properties such as compressive strength, flexural strength, carbon uptake were respectively measured. Six bricks for each property were tested immediately after 3 h mineralization and the data were averaged.

The micro-morphology, mineralogical compositions analysis, pore structure analysis and thermal analysis on the bricks were conducted by using FEI Sirion Scanning electron microscope (SEM), Bruker D8-Discover X-ray powder diffractometer (XRD), Micromeritics Autopore IV9510 Mercury Porosimetry (MIP) and NETZSCH STA449F3 simultaneous thermal analysis meter (DTA/TG) respectively.

## 3. Results and discussion

### 3.1. Properties

#### 3.1.1. Strength

The effect of slaked lime content and bacterial powder on the strength of steel slag bricks was shown in Fig. 4. As shown in Fig. 4, bacterial powder has little effect on the strength of steel slag bricks. However, through the mineralization process with the bacterial powder can make the compressive strength and flexural strength of steel slag bricks higher than the mineralization process only, which indicated that bacterial powder could accelerate the rate of carbon sequestration in mineralization process. Besides, at a low content of slaked lime, the compressive and flexural strength increased with the content of slaked lime, when the slaked lime content within the range of 0.1–0.3, the strength growth was particularly evident. But when the lime content was greater than 0.3, continue to increase the lime content, compressive and flexural strength remained unchanged.

#### 3.1.2. Carbon uptake

Carbon uptake was determined using the mass gain method by measuring the sample mass before and after mineralization. The mass difference was assumed to represent the carbon dioxide uptake Eqs. (4).

$$\text{Carbon uptake} = \text{Mass}_{\text{after mineralization}} + \text{Water}_{\text{lost}} - \text{Mass}_{\text{before mineralization}} \tag{4}$$

In addition, the strength of micarbial mineralized steel slag bricks and mineralization mass change has a positive correlation (Fig. 5), it was feasible to use the mass change to measure the strength of the steel slag products roughly.