



The Properties of the Microbial Carbon Sequestration Brick Made of Steel Slag-Slaked Lime Mixture

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ABSTRACT

Mineral CO₂ sequestration, carbonation of alkaline silicate Ca minerals is a possible technology for the reduction of carbon dioxide emissions to the atmosphere. Microbially induced carbonate precipitation technology is a latest progress in bio-mineralization. In this paper, the properties of the microbial carbonated brick made of steel slag-slaked lime mixture such as strength, drying shrinkage, water absorption and soundness were investigated. The optimal slaked lime/steel slag (SL/SS) ratio for the microbial carbonated brick made of steel slag-slaked lime mixture is 0.3. The microbes in the brick were able to survive in the high alkali environment of Steel Slag-slaked Lime Mixture for a period of time, and maintain the enzyme activity. The XRD and pore structure analyses indicate that the properties of the microbial carbonated brick are suitable for the formation of the carbonate crystal. Meanwhile the CSH gel in the bricks provides a source of calcium carbide reaction, the resulting calcium carbonate-filled voids in body and cementation, optimized pore structure and increase strength. The experimental results indicate that, when the dosage of microorganisms was 1%, the strength of the brick could increase 50%, its drying shrinkage reduces, and its soundness becomes eligible. Microbes could induce the deposition of CaCO₃ efficiently with the dissolution of Ca²⁺ in the Steel Slag-slaked Lime Mixture. The role of microorganisms are loading and catalyst, it could transport a steady which stream carbon dioxide into the body inside the carbonization reaction, meantime, the secretion of the enzyme can significantly accelerate the hydration rate of carbon dioxide, which is formed inside the body more CO₂-, Ca²⁺ has a higher probability combine with CO₂- to generate CaCO₃.

INTRODUCTION

During steel manufacturing, a significant amount (10%-15%) by weight of the used in China [Proctor, 2000]. Huge amount of the unused slag takes up land and pollutes the environment. Fortunately, steel slag is rich of CaO and MgO, (34%-52%),[Li ,2011].which are regarded as ideal feedstocks for CO₂ sequestration. Therefore, many studies have been conducted on the utilization of steel slag for CO₂ sequestration. [Shi , Huijgen , Lekakh ,2000,2011,2008] However, most of those studies were carried out with aqueous method, use solution to leach Ca²⁺ and Mg²⁺ from steel slag, and sequester CO₂ with the reaction between CO₂ and these ions,[Bonenfant D ,2008]. Since the carbonated slag produced with this method exhibits poor activity and exists as slurry, it is even more difficult to be used than the steel slag, and thus those studies do not address the disposal problem of steel slag [Kodama S, 2008]. Biological mineralization as a common phenomenon in nature is a process of solid phases of various materials with special advanced structures assembled in biological systems [P. Ghosh,S.S. Bang,V.Wiktor, H.M,2005,2001,2011]. During this process, organic macromolecules and inorganic ions interact in the interphase which enables the biogenic mineral to have a special multiscale structure and assembly regulating inorganic mineral face separated from the molecular level[H.M. Jonkers,W.L. Nicholson ,2010,2011].

In this paper, an appropriate mineralization bacteria has been selected, for example, for the use of the enzymatic effect in the growth and reproduction process to decompose a specific substrate and the addition of Ca²⁺ to form (CaCO₃) in a certain time, which has a nano-level spherical cluster on its surface. In addition, the morphology, structure, and thermal decomposition properties of the hydroxyapatite precipitates were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD).

EXPERIMENTAL

Raw materials. Steel slag (SS) with specific surface area of 400 m²/kg and density of 3070 kg/m³ from Bao Steel Company and slaked lime (SL) with solid content of 50% made by the hydrolysis of CaO from the byproduct of the soda production were used. Its chemical composition, obtained from X-Ray Fluorescence (XRF) Analyzer, is presented in Table 1. River sand with modulus of 2.26 and bulk density of 1.47 kg/m³ as used as aggregates.

Fig.1 is the XRD patterns of steel slag. As shown in Fig. 1, steel slag contains some C₂S, but due to the lack of C₃S and the presence of large amount of iron oxides which has no cementitious properties, its hydraulic activity is rather low. Furthermore, steel slag also contains some f-CaO which could result in the uncontrolled volume expansion.

Table 1. Chemical Compositions of Steel Slag (wt/%)

Compositions	CaO	SiO ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃	P ₂ O ₅	SO ₃
Content	43.7	13.1	5.1	0.0	27	7.2	0.6

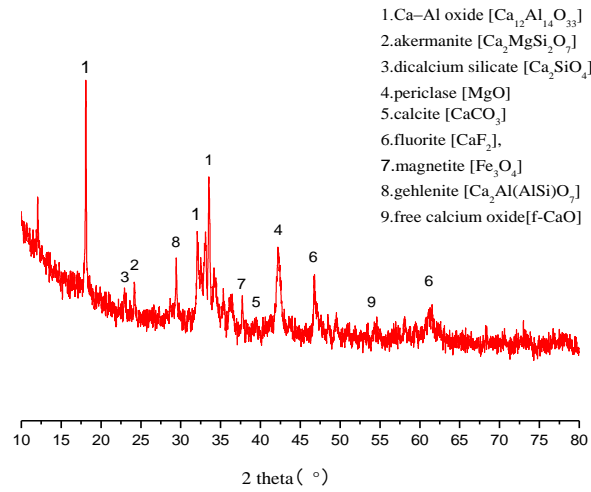


Figure 1. X-ray Diffractograms of Steel Slag

Sample preparation. 5 mix-proportions by varying the Bacterial Powder ratio (by dry weight) are given in Table 2. Their water/binder (SS+SL) ratio and sand/binder ratio are fixed at 0.5 and 2.0 respectively. The raw materials were mixed with water for 4min first, and then were cast into moulds of 40mm×40mm×160 mm. All samples were demoulded after 24h curing at 60% ± 5%RH and 20 ± 5°C. In order to further investigate the mechanism and the environmental benefits of the carbonated brick, paste samples were used for the sake of eliminating the aggregate effect. The paste samples were prepared through the same procedure.

Table 2. Mix Proportions (g)

Mix	SS	SL	Water	Aggregate	Bacterial Powder	Curing Condition
S1	525	105	315	1250	0	standard
S2	525	105	315	1250	3.15	standard
S3	525	105	315	1250	6.3	standard
S4	525	105	315	1250	9.45	standard
SP1	525	105	315	1250	0	carbonation
SP2	525	105	315	1250	3.15	carbonation
SP3	525	105	315	1250	6.3	carbonation
SP4	525	105	315	1250	9.45	carbonation

During the carbonation experiment, the slag bricks was placed into the reactor. The diagram of carbonation activation setup are shown in Fig.2. Then the autoclave was sealed and vacuumized until the interior pressure to 0.02MPa by the vacuum pump. The autoclave was replenished with CO₂ to reach the specified pressure after vacuumized. The operating pressure of reactor was 3 bar, and temperature was 25C, RH% was about 70%, Carbonated bricks were cured for 4h in the reactor. The samples without

carbonation were curing in a standard environment with RH $95\pm 5\%$ and $20^{\circ}\text{C}\pm 2^{\circ}\text{C}$. When the bricks were carbonated, the strength of all the samples were tested.

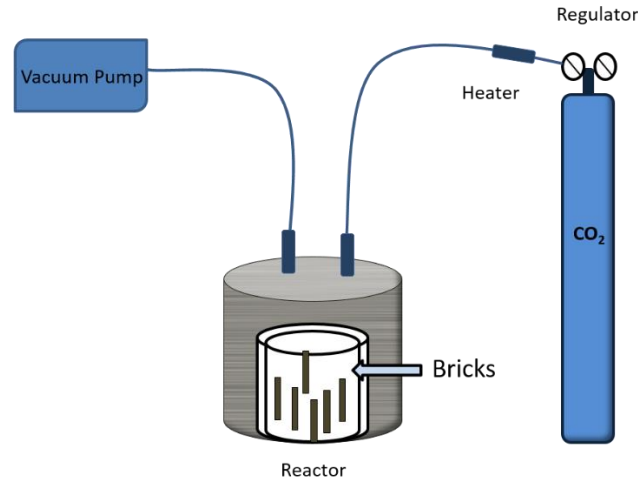


Figure 2. Carbonation Activation Setup

Test methods. X-ray techniques (XRD, Bruker Company, Germany) analysis was carried out on sandstones at room temperature by a D8-Discover X diffraction meter (40 kV, 40 mA) with Cu ($\lambda=1.5406 \text{ \AA}$) irradiation at the rate of 0.15 s/step in the range of 5° – 90° . SEM (FEI Company, Netherlands) with a GENESIS 60S energy dispersive X-ray spectroscopy (EDS) spectroscopy system with magnification from 10,000 to 100,000 was used to observe the morphology and to measure the elemental compositions of the precipitation. The accelerating voltage and spot size of the secondary electron detector were 20 kV and 4.0, respectively.

RESULTS AND DISCUSSION

Strength. The effects of the bacterial powder ratio on the strength of carbonated and un-carbonated bricks are shown in Table 3. The strength of un-carbonated brick increases with the bacterial powder ratio, when the adding quantity reached the maximum at the 1.5%, the compressive strength of S4 reached to 3.5MPa, however, when the adding quantity is 0, the compressive strength of S4 is only 1.2MPa. With the 1.5% of bacterial powder, the compressive strength improved about 3 times. The same tendency is observed in the case of carbonated bricks. When the adding quantity reached the maximum at the 1.5%, the compressive strength of SP1 reached to 17.5MPa. With the 1.5% of bacterial powder under carbonated condition, the compressive strength improved about 70%. Furthermore, it should be noticed that the carbonated bricks exhibit much higher strength than the un-carbonated ones.

Table 3. Strength of bricks for different curing condition

Mix	compressive strength/MPa	flexural strength /MPa
S1	1.2	0.35
S2	1.7	0.6
S3	2.9	0.9
S4	3.5	1.2
SP1	10.8	1.5
SP2	14.7	2.7
SP3	16.8	3.5
SP4	17.5	3.7

XRD analysis. X-ray diffractograms of slag brick are showed in Fig. 3. After the activation of slaked lime, as shown in the XRD pattern, the peaks of $\text{Ca}(\text{OH})_2$ become strong, revealing that only a few of $\text{Ca}(\text{OH})_2$ in the slaked lime participates in the activation on steel slag. With the addition of bacterial powder, the peaks of $\text{Ca}(\text{OH})_2$ become weaker, Microbes could induce the deposition of CaCO_3 efficiently with the dissolution of Ca^{2+} in the Steel Slag-slaked Lime Mixture. After carbonation, as shown in the XRD pattern, the peaks of $\text{Ca}(\text{OH})_2$ disappear, those of C_2S and C-S-H become much weaker, while peaks of CaCO_3 are distinct, indicating that $\text{Ca}(\text{OH})_2$, C_2S and hydration products are carbonated and transformed into CaCO_3 . Form the diffractograms of bricks after carbonated, there was the peak of calcium carboaluminate.

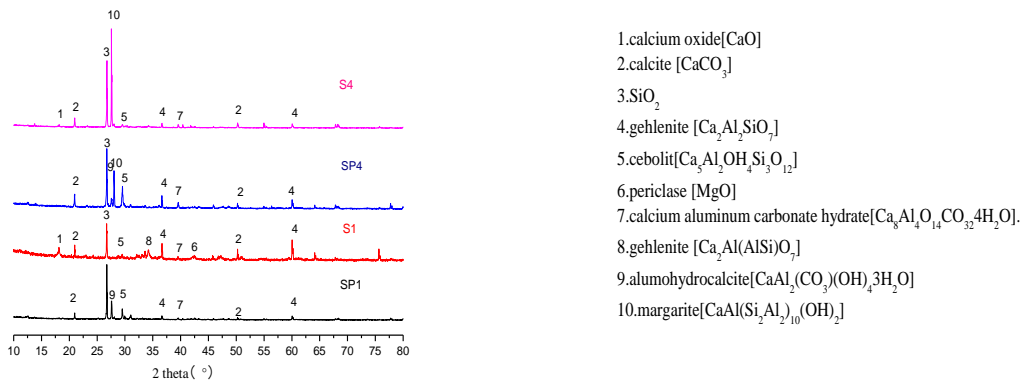


Figure 3. X-ray Diffractograms of Slag Brick after Carbonation

SEM analysis. SEM and EDS analysis of the samples curing in carbonated condition are shown in Fig. 4 and Table 4. As SEM images show, the overall evaluation of the morphology of the samples indicates a suitable and uniform distribution of particles of calcite (CaCO_3) crystal composites, The internal structure of carbonated bricks is compacted, calcite crystal form in high pressure arranges closely, crystallinity is better, crystalline size is greater, which contributed high strength. EDS showed that in the internal structure of carbonated bricks, calcite distributed uniformed in the bricks which contributed the strength obviously. Meanwhile, there were hexagonal prism shape crystal form in the samples, EDS showed that

calcium hydroferrocarbonate ($C_3A \cdot FeCO_3 \cdot 11H_2O$) has formed during the hydration of carbonated slag bricks, it may contribute to the increase of the compressive strength in later ages.

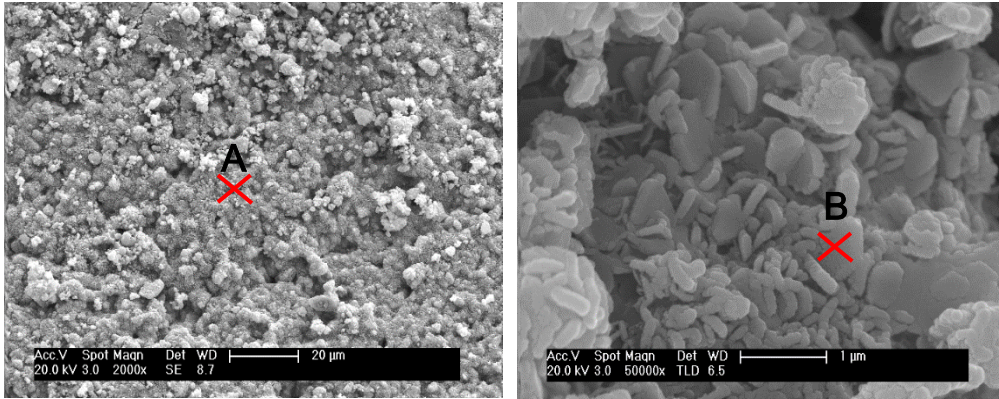


Figure 4. SEM image of carbonated slag brick with bacterial powder

Table 4. EDS analysis of point A and B

Element	Ca	Fe	O	C	Al	Si
A	45.74	3.75	35.91	14.55	0	0
B	22.02	14.56	41.41	13.29	4.84	3.87

CONCLUSION

The optimal slaked lime/steel slag (SL/SS) ratio for the microbial carbonated brick made of steel slag-slaked lime mixture is 0.2. The microbes in the brick were able to survive in the high alkali environment of Steel Slag-slaked Lime Mixture for a period of time, and maintain the enzyme activity. The XRD analyses indicate that the properties of the microbial carbonated brick are suitable for the formation of the carbonate crystal. Meanwhile, the CSH gel in the bricks provides a source of calcium carbide reaction, the resulting calcium carbonate-filled voids in body and cementation, optimized pore structure and increase strength. The experimental results indicate that, when the dosage of microorganisms was 1.5%, the strength of the brick could increase 70%, and its soundness becomes eligible. Microbes could induce the deposition of $CaCO_3$ efficiently with the dissolution of Ca^{2+} in the Steel Slag-slaked Lime Mixture. The role of microorganisms is loading and catalyst, it could transport a steady which stream carbon dioxide into the body inside the carbonization reaction, meantime, the secretion of the enzyme can significantly accelerate the hydration rate of carbon dioxide, which is formed inside the body more CO_3^{2-} , Ca^{2+} has a higher probability combine with CO_3^{2-} to generate $CaCO_3$.

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