Effect of Moisture Content on CO_2 Sequestration by BOF Slag in Landfill Cover

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ABSTRACT

Among many anthropogenic sources of greenhouse gases (GHG), landfill emissions, consisting of methane (CH_4) and carbon dioxide (CO_2), are one of the major contributors of anthropogenic GHG. In recent years, various innovative landfill biocovers have been investigated and developed to mitigate the emissions of methane (CH_4) from municipal solid waste (MSW) landfills. However, the problem of CO_2 emissions [which constitute about 40% of landfill gas (LFG)] from MSW landfills still remains unresolved. An innovative cover system which consists of basic oxygen furnace (BOF) slag with biochar amended soil is being developed to mitigate CH_4 and CO_2 emissions from landfills. The biochar amended soil is effective in mitigating CH_4 emissions by microbial methane oxidation, while BOF slag could be effective in sequestering CO_2 emissions by carbonation mechanisms. However, the properties of BOF slag vary based on several factors such as mineralogical composition of slag, particle size, moisture content, and temperature. In this study, CO_2 sequestration potential of BOF slag was evaluated under synthetic LFG condition. The performance of the BOF slag in sequestering CO_2 under different moisture condition was also examined. The results showed that BOF slag can sequester substantial amount of CO_2 under LFG condition. The study also enlightened the importance of moisture for initiating carbonation reaction; however, the moisture alone was not the controlling parameter for CO_2 sequestration. The mineralogy of the BOF slag plays an important role in determining CO_2 sequestration capacity of the slag.

INTRODUCTION

Municipal solid waste (MSW) landfills are one of the major sources of the anthropogenic greenhouse gases like methane (CH_4) and carbon dioxide (CO_2). In the U.S., MSW landfills are the third largest source of anthropogenic CH_4 emissions which contributed to 14.1 percent of those emissions in 2016 (US EPA, 2018). In the recent years, a number of studies have focused on the mitigation of CH_4 emissions from MSW landfills in the form of organic amendments like biocovers. Biocovers facilitate microbial methane oxidation in the presence of oxygen thus mitigating CH_4 emissions from MSW landfills. However, bio-based amendments like compost have other limitations. Sadasivam and Reddy (2014) summarized the various studies carried out on soil and bio-based cover systems and their limitations. In the course of enhancing microbial methane oxidation to mitigate CH_4 emissions, biochar amended cover soils have shown promising results (Reddy et al. 2014; Yargicoglu and Reddy, 2017a, b; Yargicoglu and Reddy, 2018). While the problems of fugitive CH_4 emissions have been dealt with, not much consideration has been given to the mitigation of the fugitive CO_2 emissions, which comprise around 50% of the landfill gas (LFG). Recently, Reddy et al. (2018a) proposed the concept of innovative biogeochemical soil cover, which can mitigate both CO_2 and CH_4 emissions from MSW landfills.

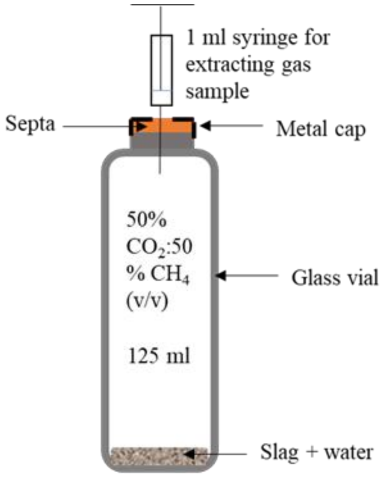

Figure 1: Schematic of batch experiment

Many studies have reported the CO_2 sequestration potential of alkaline industrial residues. Slags from steel making are alkaline, rich in calcium, and have demonstrated significant CO_2 sequestration potential (Huijgen et al. 2005; Bonenfant et al. 2008). Among the various types of steel making slags (basic oxygen furnace (BOF), electric arc furnace (EAF), ladle furnace (LF)), BOF slags have shown promising CO_2 sequestration potential (Chang et al. 2011). Chang et al. (2011) also evaluated the carbonation potential of steel slag under different operational conditions such as reaction time, temperature, and CO_2 flow rate. Liquid to Solids ratio (L/S ratio) also has been an important parameter affecting carbonation of steel slag. Different studies have reported different values of optimum L/S ratios for carbonation of steel slags based on their experimental conditions (Huijgen et al. 2005; Baciocchi et al. 2009; Sarperi et al. 2014, and Reddy et al. 2018b). However, many of these studies simulated industrial processes which are quite different than landfill conditions.

In this study, the authors investigated the effects of moisture (expressed by L/S ratios) on the CO_2 sequestration capacity of BOF slag exposed to simulated landfill gas conditions (50% CO_2 and 50% CH_4). The main aim of the study was to examine the performance of the BOF slag in CO_2 sequestration under various moisture conditions that may prevail in the landfill cover due to seasonal variations.

MATERIALS AND METHODS

Material Characterization

The BOF slag used in this study was obtained from Indiana Harbor East Steel Mill (supplied by the Phoenix Services, LLC). The BOF slag was crushed and screened at the plant with a maximum size of 10 mm before being supplied to the laboratory for the study. The physical and geotechnical characterization of the BOF slag was carried out following ASTM standard procedures. The specific gravity of the BOF slag was determined as per the ASTM D854 standard procedures. The grain size distribution was obtained from sieve analysis following ASTM D422 standard procedures. The water holding capacity was measured following standard procedures as per ASTM D2980. The loss on ignition value was obtained according to the ASTM D2974 standard procedures. The pH of the BOF slag was measured using an ORION Model 720A pH meter at a liquid to solid ratio of 1:1. The electrical conductivity of the BOF slag was measured using a Corning 311 Conductivity meter.

Table 1: Physical and geotechnical properties of BOF slag

Properties	Method	BOF slag
Specific Gravity	ASTM D854	3.46
Grain Size Distribution:	ASTM D422	
Gravel (%)		20.8
Sand (%)		74.2
Fines (%)		5.0
D_{50} (mm)		1.5
C_c		0.7
C_u		18
USCS Classification	ASTM D2487	SP-SM
Water Holding Capacity (w/w)	ASTM D2980	20
Loss on Ignition (%)	ASTM D2974	1.6
pH (at L/S of 1:1)	ASTM D4972	12.1
Electrical Conductivity (mS/cm)	ASTM D4972	13.3

The chemical/mineralogical characterization of the BOF slag was achieved by X-ray powder diffraction and Rietveld quantification analyses. The morphological characterization of the BOF slag before and after carbonation was carried out by Scanning Electron Microscopy (SEM) analysis. The SEM analysis was performed by a JEOL JSM-6320F High Resolution Scanning Microscope.

Batch Experiments

Batch experiments were performed on the as-received BOF slag samples. Four 1 g specimens of oven dried BOF slag were mixed with 0, 0.1, 0.15 and 0.2 g of deionized water in four 125 ml glass vials to obtain the L/S ratios of 0, 0.1, 0.15 and 0.2. The upper limit of the moisture content used in the experiment was chosen based on the water holding capacity of the slag which was 20% (w/w). The glass vials with BOF slag were purged with synthetic LFG mixture (50% CO_2: 50% CH_4 (v/v)) under normal atmospheric condition and room temperature. Immediately after purging, the vials were sealed with a rubber septa and secured with a metal crimp cap to prevent any leakage of the gas. The vials were rigorously stirred to enhance liquid/gas mass transfer. Fig. 1 shows the schematic diagram of the batch test set up. Gas samples from each vial were analyzed by gas chromatography (GC) using a SRI 9300 GC equipped with a thermal conductivity detector (TCD) and CTR-1 column capable of separating N_2 and O_2 for simultaneous analysis of CO_2, CH_4, O_2 and N_2. One ml of gas samples from each vial were extracted in a 1 ml syringe which was then reduced to 0.5 ml before analyzing the gas sample to eliminate the pressure effects on the gas concentrations detected by GC. The GC was calibrated with three standard CH_4-CO_2 gas mixture of 5%, 25% and 50% (v/v) concentrations. Considering that most of the carbonation reactions occurred in the first few hours, the tests were performed for 24 hours, and the gas samples were analyzed at intervals of 0, 1, 3, 5 and 24 hours. All the bath experiments were performed in triplicate.

RESULTS AND DISCUSSION

Material Characterization

The physical and geotechnical properties of the BOF slags are summarized in Table 1. The grain size distribution curve is shown in Fig. 2. The grain size distribution shows that the BOF slag was silty sand type material with mean particle size of 1.5 mm. The BOF slag has low fines content. The pH of the slag is high which shows alkaline nature of the BOF slag. The loss on ignition value is low which indicates that the BOF slag has not undergone much aging and hence, is in reactive form. The specific gravity of the slag is 3.46 which is relatively high and can be attributed to the higher iron content.

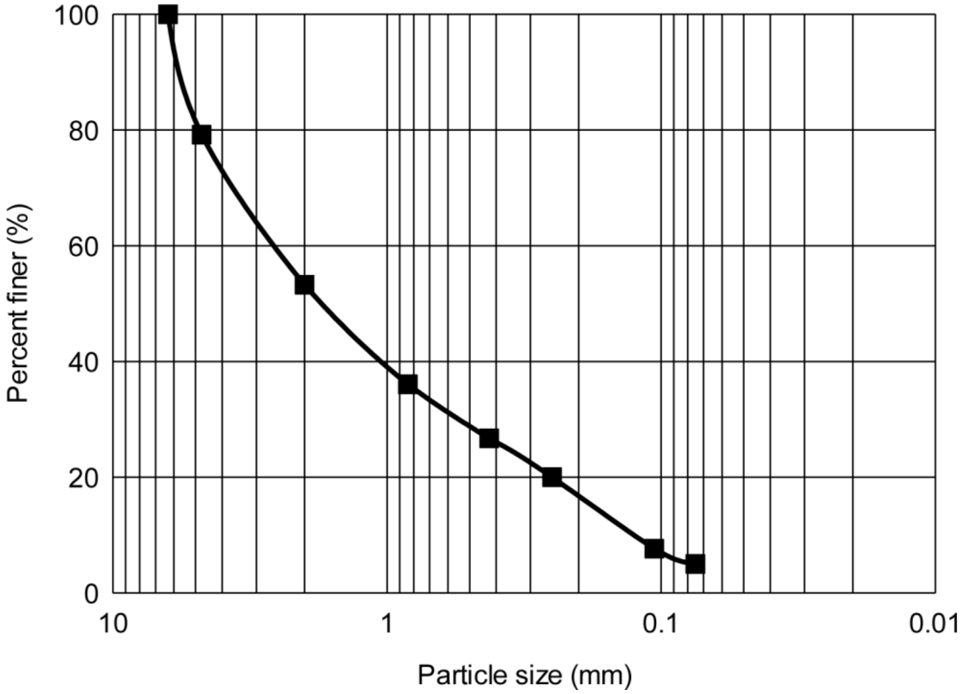

Figure 2. Grain size distribution of BOF slag

Table 2: Chemical composition (major oxides) of BOF slag

Sample	CaO (wt %)	SiO_2 (wt %)	Al_2O_3 (wt %)	Fe_2O_3 (wt %)	MgO (wt %)	SO_3 (wt %)	LOI
BOF Slag	29	10.55	3.8	22.25	9.3	0.2	3.65

Table 2 shows the major oxides present in the BOF slag, and Table 3 shows the mineralogical composition of the BOF slag. The major constituents of the BOF slag are CaO (29%), SiO_2 (~11%), Al_2O_3 (~4%), Fe_2O_3 (~22%) and MgO (~9%). High alkalinity is attributed to the high CaO content of the slag which is associated with the production process of the BOF slag. The major mineral phases present in the BOF slag are free lime (CaO, 2.4%), portlandite ($Ca(OH)_2$, ~2.5%), larnite (Ca_2SiO_4, ~12%), calcium ferrite ($Ca_2Fe_2O_3$, ~14.5%) and Mg-wuestite ((Mg,Fe)O, ~5.3%). The maximum theoretical carbonation potential of the BOF slag is 228 mg CO_2/g BOF slag which was calculated based on the total CaO content of the slag (29 wt%) and molar balance of the following reaction:

$$CaO + CO_2 \rightarrow CaCO_3 \quad (1)$$

The free lime content is relatively low in the BOF slag. The CaO is generally bound with the mineral phases in the form of calcium silicates and aluminates.

Table 3: Mineralogical composition of BOF slag

Mineral	Formula	BOF slag (wt %)
Lime	CaO	2.4
Portlandite	$Ca(OH)_2$	0-4.4
Larnite	Ca_2SiO_4	11.7-12.6
Calcite	$CaCO_3$	0.8-1.1
Srebrodolskite	$Ca_2Fe_2O_5$	14.2-15
Magnesioferrite	$MgFe_2O_4$	6-6.5
Iron Magnesium Oxide	Fe0.76Mg0.24O	5.2-5.4
Wuestite	FeO	3.4-3.5
Periclase	MgO	0.7-0.8
Brucite	$Mg(OH)_2$	0.4
Mayenite	$Ca_{12}Al_{14}O_{33}$	2-2.9
Akermanite	$Ca_2MgSi_2O_7$	2
Merwinite	$Ca_3Mg(SiO4)_2$	1.8-2.1
Katoite	$Ca_3Al_2(OH)_{12}$	1.7-1.8
Amorphous Material		43-43.7

Note: Analyzed by PMET, Inc., PA

Batch Experiments

The effect of moisture content on the CO_2 sequestration potential of the BOF slag was evaluated by performing batch experiments at different L/S ratios under landfill gas conditions (50% CH_4: 50% CO_2 (v/v)). The gas (CO_2 and CH_4) removal capacity was calculated by the difference in the initial concentration (C_{in} at t=0) and the concentration at time t (C_t) of the gas in the vial (C_{in}-C_t). The concentration of the gas (vol %) as obtained after analyzing in GC was converted to the concentration in terms of mg/l applying ideal gas law (PV=nRT). Considering volume of the gas is equal to the volume of the vial (125 ml), and the initial mass of the BOF slag taken was 1 g, the concentration of the gas was obtained in terms of mg/g as shown in Eq. (2).

$$Gas\,concentration\ (\frac{mg}{g}) = \frac{mg}{l} \times \frac{0.125 l}{1 g} \quad (2)$$

Fig. 3 (a) shows CO_2 and CH_4 removed in 24 hours. Fig. 3(a) shows negligible CO_2 removal in dry state (L/S =0) followed by significant increase in the removal in the presence of moisture. CO_2 removal shows an increasing trend from L/S of 0 to 0.15. The CO_2 removal at L/S from 0.15 to 0.2 were comparable. The BOF slag also showed some amount of CH_4 removal however, the removal is significantly lower (<10 mg/g). This could be attributed to the adsorption of CH_4 on the slag surface due to the presence of alumina (Al_2O_3) (Li et al. 1994). The 24 hours CO_2 removal capacity of the BOF slag was in the range of 32-45 mg CO_2/g BOF slag with optimum removal at L/S in the range of 0.15 to 0.2 (g/g).

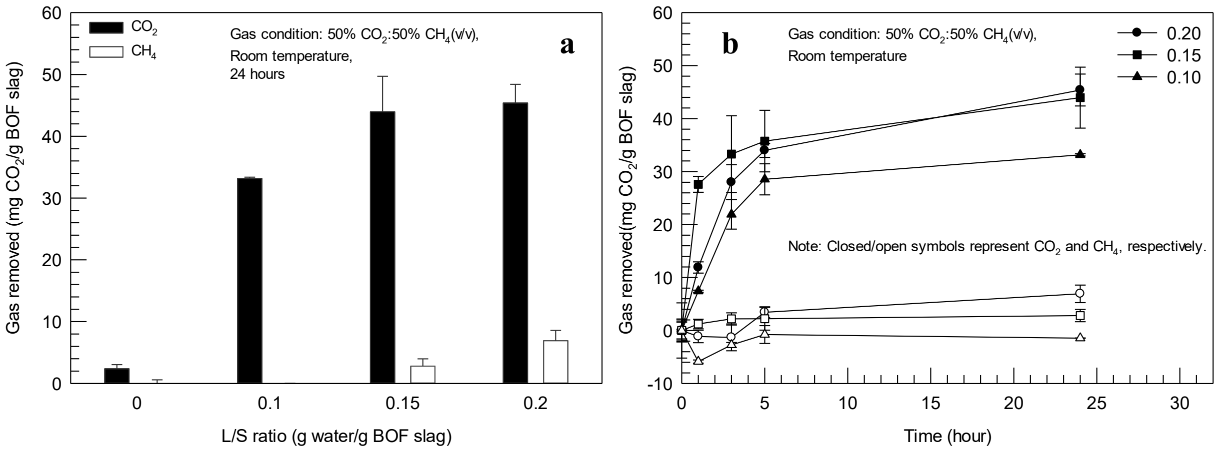

Figure 3. Effect of moisture content on the removal of CO_2 and CH_4 by BOF slag at different liquid/solid ratio (L/S) exposed to synthetic landfill gas mixture (a) cumulative removal in 24 hours (b) removal of gas at different points of time until 24 hours

Various researchers have shown different optimum L/S ratios for carbonation in their experimental conditions. Huijgen et al. (2005) showed L/S ratio of 2 (kg/kg) as the optimum moisture content for carbonation of Linz Donawitz steel slag (LD) slag in slurry phase in their reactor. At L/S ratio higher than 2 (kg/kg), they observed a reduction in degree of carbonation with increase in moisture content. Baciocchi et al. (2009) achieved the highest CO_2 removal at L/S ratio ranging from 0.3 to 0.4 l/kg for stainless steel slag exposed to 100% CO_2. Sarperi et al. (2014) achieved optimum CO_2 removal at L/S ratio in the range of 0.05 to 0.2 l/kg for BOF slag exposed to mixed gas of CO_2 and CH_4. Su et al. (2015) observed highest carbonation of BOF slag at L/S ratio of 2-10 (g/g) in their experimental conditions. These studies show variable optimum moisture content range for CO_2 removal.

Among the studies carried out by various researchers, the study by Sarperi et al. (2014) was closest to our study. The L/S ratio for maximum CO_2 removal reported by Sarperi et al. (2014) was 0.1 l/kg whereas our study showed maximum CO_2 removal at L/S ratio of 0.2 g/g. Study by Reddy et al. (2018) also showed maximum CO_2 removal at a moisture content of 10% (w/w) or L/S ratio of 0.1 g/g. The difference could be due to the difference in the mineralogy of the BOF slag under study. The BOF slag used by Reddy et al. (2018) had a higher $Ca(OH)_2$ content (9.5%) in comparison to the BOF slag used in this study (2.2%). For the BOF slags having higher amount of hydrated oxides like $Ca(OH)_2$, a higher degree of carbonation may happen at lower moisture content as the moisture added would be used in dissolution of CO_2 and leaching of Ca^{2+} ions than hydration of the other minerals (Baciocchi et al. 2009).

Fig. 3(b) shows the removal of CO_2 and CH_4 at different points of time until 24 hours at L/S ratios ranging from 0.1 to 0.2 (g/g). The initial steep slopes of the curves show that the carbonation reaction was fastest in the first 5 hours followed by a relatively slower reaction rate. Free lime (CaO), $Ca(OH)_2$ and Ca_2SiO_4 are the most reactive mineral phases for carbonation (Huijgen et al. 2005; Bonenfant et al. 2008; Uibu et al. 2011 and Su et al. 2016). The maximum CO_2 sequestration by the BOF slag after 5 hours was nearly 35 mg/g and after 24 hours was 45 mg/g. The theoretical CO_2 sequestration capacity based on the amount of [CaO (2.2%) + $Ca(OH)_2$ (2.4%)] present in the slag was 32 mg/g and based on total [CaO (2.2%) + $Ca(OH)_2$ (2.4%) + Ca_2SiO_4 (12%)] was 93 mg/g . The theoretical CO_2 sequestration capacity was calculated based on the molar balance of the following reactions.

$$CaO(free\,lime) + CO_2 \rightarrow CaCO_3 \quad (3)$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (4)$$

$$Ca_2SiO_4 + 2CO_2 \rightarrow 2CaCO_3 + SiO_2 \quad (5)$$

The CO_2 sequestered in the first 5 hours corresponds to the theoretical sequestration capacity of the BOF slag based on the amount of [$CaO + Ca(OH)_2$] present in the BOF slag. From these results it can be hypothesized that free lime and portlandite are the first minerals to react during carbonation reactions. The CO_2 sequestration in 24 hours exceeds the theoretical capacity of [$CaO + Ca(OH)_2$] which signifies the participation of Ca_2SiO_4 in CO_2 removal. The flatter slope of the curves after 5 hours shows slower reaction kinetics. Considering all the Ca_2SiO_4 present in the BOF slag would react with CO_2, there was only 21% carbonation conversion of Ca_2SiO_4 during the experiment. This suggests slower dissolution rate of Ca_2SiO_4 under ambient condition. The reason could be the slower reaction kinetics of Ca_2SiO_4 or the formation of a carbonate layer and silicate rims over the slag particles preventing further leaching of Ca^{2+} into the solution (Huijgen et al. 2005). Overall, the BOF slag showed 43% removal of CO_2 in 24 hours calculated based on initial and final concentration of CO_2 in the vial.

Figures 4(a) and 4(b) show the SEM images of the original and carbonated BOF slag from the batch experiment, respectively. The non-carbonated BOF slag sample showed smooth surface with particles far apart and relatively more porous surface, whereas the carbonated sample showed formation of needle like outgrowths covering the pores. These outgrowths were recognized as carbonate crystals formed from carbonation reactions (Huijgen et.al. 2005; Chang et.al. 2011).

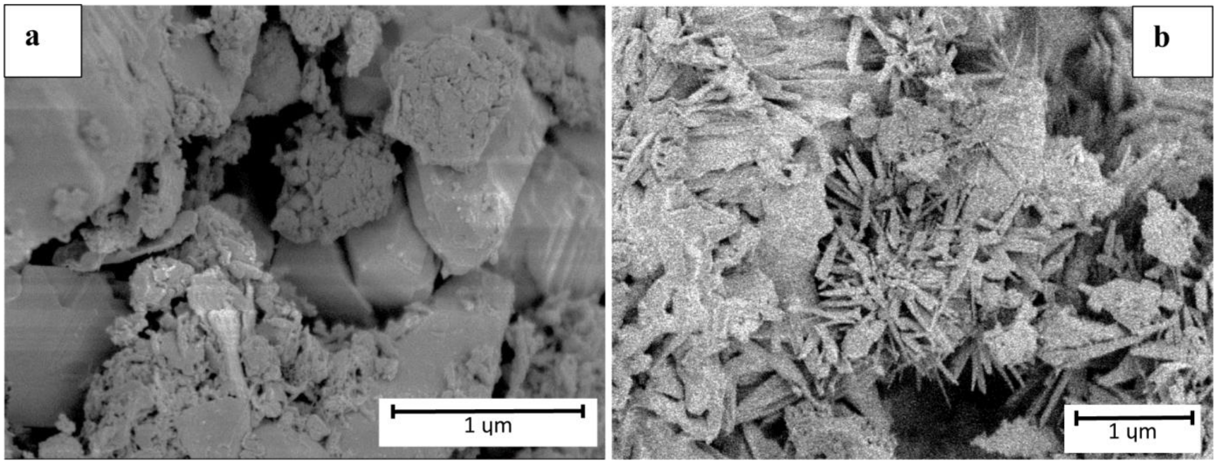

Figure 4. SEM images of BOF slag (a) Original (b) Carbonated

CONCLUSION

The CO_2 sequestration potential of the BOF slag exposed to synthetic landfill gas (50% CO_2: 50% CH_4 (v/v)) was evaluated at different moisture conditions. The results showed that the moist BOF slag can sequester considerable amount of CO_2 under landfill gas condition. Moisture was found to be a key parameter for the carbonation reaction as the BOF slag showed negligible CO_2 sequestration in a dry state (L/S ratio of 0 g/g) whereas, a substantial increase was observed in the moist state (L/S ratio of 0.1 to 0.2 g/g). In the moist state, the dissolution rates of the minerals present in the BOF slag play an important role in CO_2 sequestration. CO_2 sequestration by BOF slag at different moisture content involves interplay between various minerals and their reaction mechanisms which needs to be confirmed with further detailed study on the dissolution characteristics as well as the reaction kinetics of the minerals present in the BOF slag. The study suggests that the BOF slag can be a potential alternative for landfill cover material to partially mitigate fugitive landfill CO_2 emission.

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