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CO₂ uptake response by BOF slag in landfill cover

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ABSTRACT: Landfill emissions like methane (CH₄) and carbon dioxide (CO₂) are one of the major contributors of anthropogenic greenhouse gases (GHG). In recent years, various innovative landfill biocovers have been investigated and developed to mitigate the emissions of methane (CH₄) from Municipal Solid Waste (MSW) landfills. However, the problem of CO₂ 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 CH₄ and CO₂ emissions from landfills. The biochar amended soil is effective in mitigating CH₄ emissions by microbial oxidation whereas, BOF slag is effective in sequestering CO₂ emissions by carbonation mechanisms. In this study, small column experiment was conducted with BOF slag under simulated landfill gas conditions (humid, 50%CO₂:50%CH₄) to analyse the gas transport and CO₂ sequestration potential of BOF slag. The results from small column test show that there is significant uptake of CO₂ by BOF slag. However, the CO₂ sequestration potential of BOF slag depends upon various factors among which mineralogical composition is a decisive parameter for the amount of CO₂ sequestered. Amount of free lime, portlandite and larnite present in a BOF slag plays a vital role in CO₂ sequestration potential.

1 INTRODUCTION

Municipal solid waste (MSW) landfills are the source of various harmful emissions like CH₄, CO₂, H₂S and nonmethane hydrocarbons (NMHC). MSW decomposes anaerobically producing large amount of CH₄. Currently, MSW landfills are the third largest source of anthropogenic methane emissions in the United States (USEPA, 2018).

Modern engineered landfills are equipped with gas collection systems to capture the landfill gases (LFG). However, the gas collection systems are not 100 % efficient. The gas collection efficiency generally varies from 60-90 % depending on the system design and effectiveness (USEPA, 2018). Hence, significant amount of LFG are still emitted into the atmosphere.

Large number of studies have focused on mitigation of fugitive landfill CH₄ emissions in the recent past. In this regard, various alternative cover systems have been developed such as biocovers which incorporate organic materials like compost, sewage sludge, peat, etc. in order to enhance microbial CH₄ oxidation (Sadasivam & Reddy 2014). Recently, biochar amended soil cover have been introduced and have shown enhanced CH₄ oxidation as the biochar provides favourable environment for dwelling of the CH₄ oxidising bacteria like methanotrophs (Reddy et al.

2014). While enormous amount of work has been done in mitigating fugitive landfill CH₄ emissions, not much attention has been given to landfill CO₂ emissions which comprises 50% of the LFG composition (USEPA 2018).

Recently, Reddy et al. (2018a) proposed a concept of biogeochemical soil cover which uses basic oxygen furnace (BOF) slag along with biochar-amended soil to mitigate LFG emissions leading to zero-emissions landfill. Steel slag is a byproduct of steel making process which is alkaline and rich in calcium (Yildirim & Prezzi 2011). BOF slag is a type of steel slag which is found to have significant CO₂ sequestration potential (Huijgen et al. 2005, Chang et al. 2011, Su et al. 2016). Past studies have focused on CO₂ sequestration of steel slag by optimizing carbonation conditions such as moisture, CO₂ pressure, temperature, etc. (Huijgen et al. 2005, Chang et al. 2012, Ko et al. 2015, Su et al. 2016). None of the studies have studied the carbonation potential of the slag under landfill conditions.

The study by Reddy et al. (2018b) showed significant CO₂ removal potential in the BOF slag under LFG conditions (50 % CH₄ and 50 % CO₂). In their study, column tests were conducted on BOF slag with continuous dry inflow LFG. However, owing to the large amount of moisture present in the landfill waste,

the LFG tends to be humid. Hence, it is crucial to examine CO₂ removal under humid flow conditions.

In this study, the CO₂ removal potential of BOF slag was investigated under simulated landfill conditions (humid, 50 % CH₄ and 50 % CO₂). A column experiment was performed under continuous LFG flow condition to estimate the maximum CO₂ removed by the BOF slag as well as to understand the factors affecting the CO₂ removal in simulated LFG conditions.

2 MATERIALS AND METHODS

2.1 BOF slag characterization

The BOF slags used in this study was obtained from the Indiana Harbor East Steel Mills in Indiana. The BOF slag was sampled in September 2017. The slag sample was received in a crushed granular form with top sieve size of 10 mm (3/8 inch). A gas mixture of 50 % CH₄ and 50 % CO₂ by volume (Praxair Distribution, Inc., Illinois) was used as simulated LFG for the experiments performed in this study.

Specific gravity, particle size distribution, soil classification, water holding capacity (WHC), hydraulic conductivity, loss on ignition (LOI) and pH of the BOF slag were determined as per the corresponding ASTM standards as shown in Table 1.

Mineralogical composition of the BOF slag was determined by X-ray powder diffraction (XRD) and Rietveld quantification analyses.

Morphological microstructure analyses were performed using scanning electron microscope (SEM). For SEM analysis, smaller grain mounds were prepared with slag samples before and after carbonation and sputter coated with 20 nm Pt/Pd using Cressington HR208 sputter coater to omit charging of particles during analysis. The SEM analyses were performed by a JEOL JSM-6320F High Resolution Scanning Microscope operated at 2.5 kV.

2.2 Column experiment

The column experiment was conducted under humidified, simulated LFG gas mixture conditions. The experiment was performed at room temperature (± 2 °C) in acrylic glass column with an inner diameter 2.5 cm and height 30 cm. The BOF slag sample was mixed with deionized water (to yield moisture content of 10%) and was placed in the column in approximately 5 cm lifts followed by light tamping. The synthetic LFG at a pressure of approximately 40 kPa was passed through a water column to humidify (not measured) the gas before introducing it into the column. Flow meters (Cole-Parmer, Model No. PMRI-010874) were connected at the column inlet and outlet to control the influent gas flow rates (10-12 ml/min) and measure the effluent gas flow rate. Gas sampling ports were connected to the inlet and

outlet of the columns to allow measurement of the influent and effluent gas concentrations. The experimental set up is shown in Figure 1. Gas samples were collected at regular time intervals from inlet and outlet sampling ports and analysed by an SRI 9300 GC equipped with a thermal conductivity detector (TCD) and CTR-1 column capable of separating CH₄ and CO₂.

3 RESULTS AND DISCUSSION

3.1 Characterization of BOF slag

The physical, geotechnical and chemical properties of the BOF slag are summarized in Table 1. The slag had majority of sand-sized particles with an average particle size of 1.5 mm. The specific gravity of the slag was high (3.46) which can be attributed to the high iron content. The water holding capacity of the slag was 20%. The slag showed low LOI value indicating that the slag has not undergone much aging and still has significant reactivity. The pH of the slag was 12.1 which renders high alkalinity to the slag.

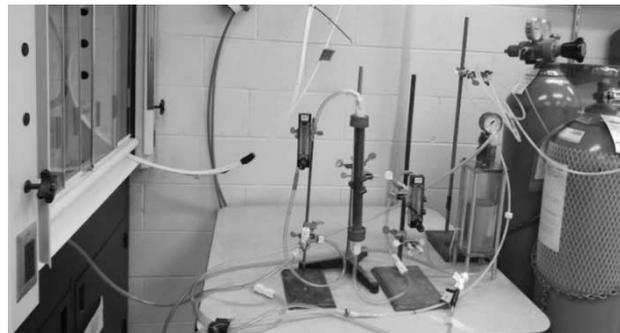


Figure 1. Experimental set up for column test

Table 1. Physical, geotechnical and chemical properties of the BOF slags

Properties	ASTM Method	BOF slag
Specific Gravity	D854	3.46
<i>Grain Size Distribution:</i>	D422	
Gravel (%)		20.8
Sand (%)		74.2
Fines (%)		5.0
D ₅₀ (mm)		1.5
C _c		0.7
C _u		18
<i>Atterberg Limits:</i>	D4318	
Liquid Limit (%)		Non-
Plastic Limit (%)		Plastic
Plasticity Index (%)		
USCS Classification	D2487	SP-SM
Water Holding Capacity (w/w)	D2980	20
Hydraulic Conductivity (cm/s), at dry density of 1.72 g/cm ³	D2434	1.1 x 10 ⁻³
Loss on Ignition (%)	D2974	1.6
pH (L/S = 1:1)	D4972	12.1

The BOF slag composition in terms of major oxides and the mineral phases is presented in Table 2 and 3, respectively. The major oxides present are consistent with the ranges given by Shi (2004). The major mineral phases determined by QXRD were free lime, portlandite ($\text{Ca}(\text{OH})_2$), larnite (Ca_2SiO_4), and calcium ferrite ($\text{Ca}_2\text{Fe}_2\text{O}_5$). The slag contained very less amount of calcite ($\sim 1.0\%$) suggesting the sample had not undergone much aging. The slag contained 29 % of CaO, which has higher propensity for carbonation than other metal oxides. However, all the CaO is not available in the free form. It is generally bound with other oxides such as larnite, calcium ferrite, etc.

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

Material	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃
	(wt %)	(wt %)	(wt %)	(wt %)	(wt %)	(wt %)
BOF slag	29	10.55	3.8	22.5	9.3	0.2

Table 3. Chemical composition (major minerals) of BOF slag

Minerals	Mineral formula	Amount (wt %)
Lime	CaO	2.4
Portlandite	Ca(OH) ₂	0-4.4
Larnite	Ca ₂ SiO ₄	11.7-12.6
Calcite	CaCO ₃	0.8-1.1
Srebrodolskite	Ca ₂ Fe ₂ O ₅	14.2-15
Magnesioferrite	MgFe ₂ O ₄	6-6.5
Iron Magnesium Oxide	Fe _{0.76} Mg _{0.24} O	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 ₂ MgSi ₂ O ₇	2
Merwinite	Ca ₃ Mg(SiO ₄) ₂	1.8-2.1
Katoite	Ca ₃ Al ₂ (OH) ₁₂	1.7-1.8
Amorphous Material		43-43.7

Note: Analyzed by PMET, Inc., PA

3.2 Column test

Figure 2 shows percentage removal of CO₂ and CH₄ by the three BOF slag on a pore volume (PV) basis of gas flow. An initial phase of near complete CO₂ (100%) removal can be seen in Figure 2 with breakthrough occurring at nearly 30 PV (nearly 5 hours). After breakthrough, the CO₂ removal gradually decreased to nearly 0 % which is taken to be the ultimate or operational CO₂ removal capacity of the BOF slag under experimental conditions. The slag did not show complete removal of CH₄. A partial removal of CH₄ was observed in the beginning of the experiment which could be due to the adsorption of CH₄ on the slag surface.

Figure 3a shows the cumulative removal of CO₂ and CH₄ in the initial phase of the experiment. The amount of CO₂ removed at breakthrough was nearly

7 mg/g after which a slight change in slope of the CO₂ removal was observed showing reduction in the removal rate. Figure 3b shows the cumulative removal of CO₂ and CH₄ in the long-term. The BOF slag showed a total CO₂ removal of 85 mg/g until termination. The termination PV was 3,600. Figure 3b shows that a significant amount of CO₂ was removed after breakthrough but at a slower rate. The gradual decline in slope after breakthrough can be attributed to the deposition of carbonate compounds or dissolution of minerals with different reaction kinetics.

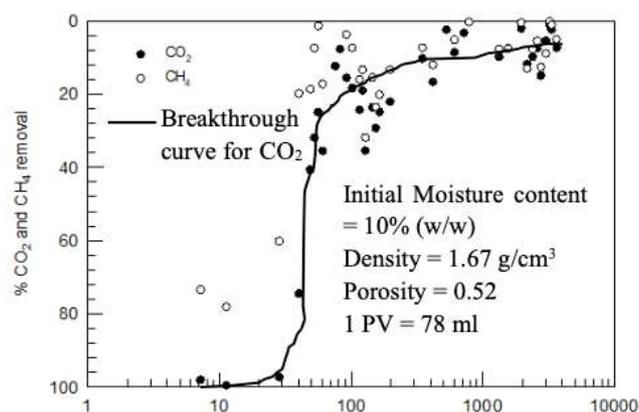


Figure 2. Percent removal of CO₂ and CH₄ by BOF slag on a pore volume basis for simulated LFG gas flow (50/50 CH₄/CO₂) at 23 ± 2°C.

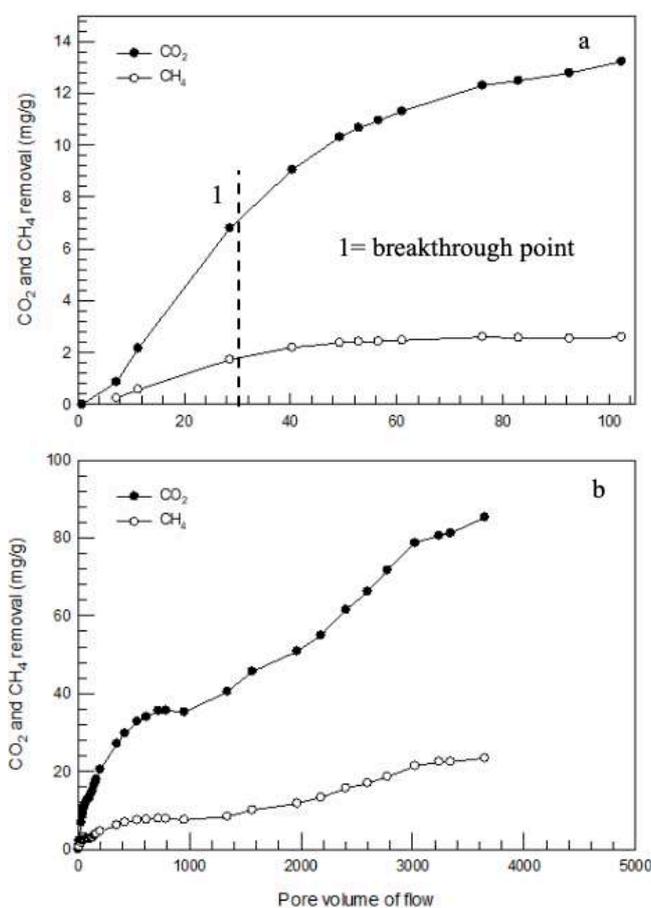


Figure 3. Short (a) and long (b) term CO₂ and CH₄ removal by BOF slag on a pore volume basis for simulated LFG gas flow (50/50 CH₄/CO₂) at 23 ± 2°C.

The theoretical CO₂ sequestration capacity of the BOF slag based on the total CaO content (29 %) of the slag is 228 mg CO₂/g BOF slag. However, not all the CaO will be available for the carbonation reaction. The freely available form of CaO is free lime and is highly reactive. Among the various Ca containing minerals present in the BOF slag, free lime and Ca(OH)₂ are the most reactive forms followed by larnite (Ca₂SiO₄) (Huijgen et al. 2005, van Zomeren et al. 2011, Su et al. 2016). Free CaO reacts with water immediately and forms Ca(OH)₂. Considering all of the free lime (~2.4%) and Ca(OH)₂ (~2.2%) present in the slag would react with CO₂, the theoretical CO₂ removal would correspond to 32 mg/g. The amount of CO₂ removed up to breakthrough was 7 mg/g which is less than the theoretical capacity (only 22% of total capacity of free lime and Ca(OH)₂). It means not all of the free lime and Ca(OH)₂ were available on the surface of the slag particles initially. As shown by the cumulative CO₂ removal curve (Figure 3b), the CO₂ removal continued gradually after breakthrough leading to a total removal of 85 mg/g until termination of the experiment. The total amount of CO₂ removed during the entire experiment exceeds the theoretical capacity of free lime and Ca(OH)₂, which clearly indicates that there were other mineral phases participating in the carbonation of the slag. The theoretical CO₂ removal capacity of Ca₂SiO₄ (~12%) is 61 mg/g. Consequently, the total theoretical capacity of the BOF slag based on the free lime, Ca(OH)₂ and Ca₂SiO₄ would be 93 mg/g which is consistent with the total CO₂ removal quantified from column experiment. Hence, it can be hypothesised that these three Ca containing minerals were contributing to the carbonation of the slag. However, other Ca containing minerals such as calcium ferrite (Ca₂Fe₂O₅) could also be simultaneously participating in the CO₂ removal, which can be confirmed with detained mineralogical analysis of the slag post carbonation which was not in the scope of this study.

In total, the BOF slag underwent 37% carbonation of the total CaO present in the slag. Degree of carbonation as high as 71% has been reported in the studies (Su et al. 2016). The degree of carbonation of 71% was obtained for BOF slag with particle size of <0.5 mm at 100°C, 250 kg/cm² and L/S ratio of 5 g/g. Whereas, our study was carried out at ambient conditions with as-received slag particles which had mean particle size of 1.5 mm, and initial moisture content of 10% (L/S ratio of 0.1 g/g). Hence, it is evident that the carbonation of slag is affected by various process variables. In the column experiment, the BOF slag was compacted in the column resulting into low porosity which could be preventing slag surfaces from being exposed to CO₂ gas thereby limiting complete carbonation of the slag. In addition, higher particle size and lesser fines content of the slag under study could also be one of the factors for a lesser degree of

carbonation. Furthermore, the formation of carbonation products such as calcite and silicate rims on the slag surface could be hindering leaching of Ca from the inner core.

3.3 SEM analysis

Figure 4 shows the morphological characteristics of the as-received and carbonated slag. The non-carbonated slag had rounded structures with particles spaced apart. The carbonated slag particles were characterized with needle or rod or plate shaped outgrowths which have been identified as calcium carbonate crystals in previous studies (Huijgen et al. 2005; Chang et al. 2011). The carbonated slag's surface was covered with carbonate crystals with lesser number of pores. This calcium carbonate coating on the slag's surface could have hindered further leaching of the Ca²⁺ from the inner core of the slag particles thereby reducing the CO₂ removal.

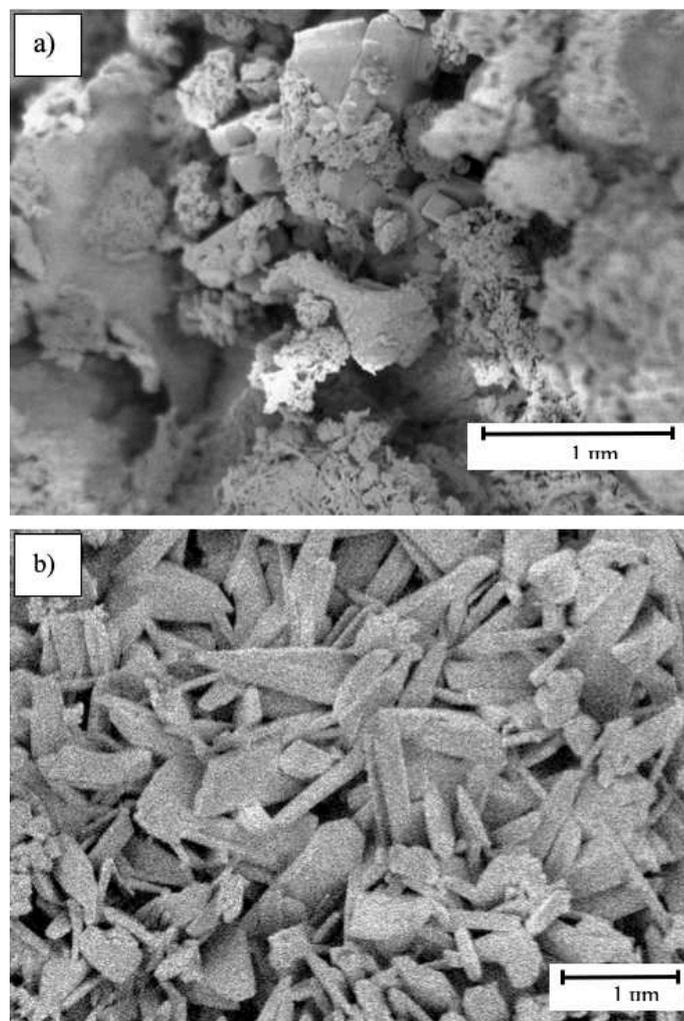


Figure 4. SEM images of a) as-received and b) carbonated BOF slag

4 CONCLUSION

This study investigated the CO₂ sequestration potential of BOF slag exposed to simulated landfill gas. The mechanism of the CO₂ removal by BOF slag was

also studied. The BOF slag showed considerable CO₂ removal potential under ambient conditions. The maximum CO₂ removal of 85 mg/g was obtained. Free lime, Ca(OH)₂ and Ca₂SiO₄ were found to be the main Ca containing minerals contributing to the CO₂ removal in BOF slag. There could be other Ca containing minerals such as Ca₂Fe₂O₅ which needs to be confirmed with further detailed mineralogical analysis post carbonation. The CO₂ removal capacity of BOF slag largely depends upon the type and amount of Ca containing minerals present in the slag. Further studies are being conducted to simulate the performance of BOF slag subjected to dynamic environmental conditions which may prevail in the landfill covers.

5 ACKNOWLEDGMENTS

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6 REFERENCES

- Chang, E.E. Chen, C.H. Chen, Y.H. Pan, S.Y. & Chiang, P.C. 2011. Performance evaluation for carbonation of steel-making slags in a slurry reactor. *J. Hazard. Mater.*, 186(1): 558-564.
- Chang, E.E. Pan, S.Y. Chen, Y.H. Tan, C.S. & Chiang, P.C. 2012. Accelerated carbonation of steelmaking slags in a high-gravity rotating packed bed. *J. Hazard. Mater.*, 227: 97-106.
- Huijgen, W.J. Witkamp, G.J. & Comans, R.N. 2005. Mineral CO₂ sequestration by steel slag carbonation. *Environ. Sci. Technol.*, 39(24): 9676-9682.
- Ko, M.S. Chen, Y.L. & Jiang, J.H. 2015. Accelerated carbonation of basic oxygen furnace slag and the effects on its mechanical properties. *Construction and Building Materials*, 98: 286-293.
- Reddy, K.R. Yargicoglu, E.N. Yue, D. & Yaghoubi, P. 2014. Enhanced microbial methane oxidation in landfill cover soil amended with biochar. *J. Geotech. Geoenviron. Eng.*, 140(9), 04014047.
- Reddy, K.R. Grubb, D.G. & Kumar, G. 2018a. Innovative biogeochemical soil cover to mitigate landfill gas emissions. *In International Conference on Protection and Restoration of the Environment XIV*.
- Reddy, K.R. Kumar, G. Gopakumar, A. Rai, R.K. & D.G. Grubb 2018b. CO₂ Sequestration using BOF slag: Application in landfill cover. *In International Conference on Protection and Restoration of the Environment XIV*.
- Sadasivam, B.Y. & Reddy, K.R. 2014. Landfill methane oxidation in soil and bio-based cover systems: a review. *Reviews in Environmental Science and Bio/Technology*, 13(1): 79-107.
- Shi, C. 2004. Steel slag - its production, processing, characteristics, and cementitious properties. *J. Mater. Civ. Eng.*, 16(3): 230-236.
- Su, T.H. Yang, H.J. Shau, Y.H. Takazawa, E. & Lee, Y.C. 2016. CO₂ sequestration utilizing basic-oxygen furnace slag: Controlling factors, reaction mechanisms and V-Cr concerns. *J. Environ. Sci.*, 41: 99-111.
- USEPA. 2018. Landfill Methane Outreach Program (LMOP). [online] <https://www.epa.gov/lmop/basic-information-about-landfill-gas> (accessed on 30 August, 2018)
- van Zomeren, A. Van der Laan, S.R. Kobesen, H.B. Huijgen, W.J. & Comans, R.N. 2011. Changes in mineralogical and leaching properties of converter steel slag resulting from accelerated carbonation at low CO₂ pressure. *Waste Manage.* 31(11): 2236-2244.
- Yildirim, I.Z. & Prezzi, M. 2011. Chemical, mineralogical, and morphological properties of steel slag. *Advances in Civil Engineering*, 2011.

