CO₂ Sequestration by Alkaline Wastes for Potential Application in the Landfill Environment

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Abstract. In order to avoid the potentially devastating consequences of global warming and climate change, the carbon dioxide (CO_2) emissions caused due to anthropogenic activities must be reduced considerably. This research examined the effect of temperature and varying proportions (0%, 25%, 50%, and 75% soil content) of soil-waste mixture on the potential of CO_2 mineral sequestration process in limiting the overall CO_2 production in landfills. The focus was on alkaline wastes like construction and demolition (C&D) waste and hospital incineration (HI) ash. Experiments were carried out in a self fabricated batch reactor at 0.4 water-to-solids (w/s) ratio, relative humidity of 60-80%, and flow rate of CO_2 at 10L/min for 2 hours for temperature variation from 25°C to 40°C at intervals of 5°C. Optimum temperature for CO_2 mineral sequestration of soil-waste mixture was found out to be 30°C. Maximum CO_2 uptake of 10.56% and 9.14% was obtained for C&D waste and HI Ash respectively at 0% soil content. Soil-waste mixture of 0% and 25% soil content was established to be best suited for CO_2 sequestration.

Keywords: Mineral Sequestration, alkaline waste, carbonation, Construction & Demolition waste.

1. Introduction

Climate change and global warming are the key concerns in the world today and the high levels of green house gas (GHG) emissions form a major reason for the prevalent worrying situation on this front. Since pre-industrial era, global emissions of carbon dioxide from the fossil fuel sources have increased from 280 ppm to 391 ppm in 2010 (NOAA, 2011) and are still rising. As per Energy Information Administration (EIA),the emission levels are expected to rise from 29.7 billion tons in 2007 to 33.8 billion metric tons in 2020 and 42.4 billion metric tons in 2035—an increase of 43 percent over the projection period and much of the rise is expected to occur in rapidly growing developing countries like China and India which are highly dependent on electricity for their energy.

Mineral sequestration is a method of CO_2 sequestration involving storage of CO_2 in the form of stable carbonates by reacting it with minerals. Mentioned first by Seifritz (1990) and discussed by Dumsmore (1992), this process emulates the natural weathering of rocks to carbonates over geological time periods. The ready availability of minerals in earth's crust, easy and ecologically safe disposal of carbonates and permanent nature of this technique makes this process attractive from the point of view of sequestration.

Using wastes has various advantages over the use of rock minerals as the process can be expected to be faster owing to the relatively open structure and higher specific surface area. Some of the wastes that are alkaline are Construction and Demolition waste(C&D waste), Hospital Incineration Ash (HI Ash).

C&D waste constitutes one third of the total municipal solid waste. Delhi generates about 6000 tons/day of municipal solid waste out of which 2500 tons/day is C&D waste. Major source of this waste is the ever

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growing infrastructure, the real estate sector and demolition of unauthorized sector. A majority of the sequestration efforts have been focused on the storage of CO_2 in large reservoirs such as the oceans, deep geologic formations, and terrestrial biosphere (Huijgen and Comans, 2003; and NRC, 2003). The main obstruction in the operation of mineral sequestration technology at the industrial scale are low reaction conversion, high energy intensity, slow reaction kinetics, and struggle for consideration with unconventional carbon capture technologies. (Santos *et al*., 2010).

The carbonation of CaO and Ca (OH)$_2$ progresses very rapidly and proceeds towards completion in several minutes at elevated temperature and pressure (Lackner *et al*., 1997). The highest temperature at which the carbonation occurs spontaneously depends on the CO_2 pressure and the type of mineral (Huijgen and Comans, 2003). Uptake of CO_2 increases with increasing temperature up to 60°C (at atmospheric pressure) (Bertos *et al*., 2004). A landfill produces up to 45% of CO_2 of the landfill gases. CO_2 emissions from a landfill can be controlled using the method of mineral sequestration. After dumping the landfill with the wastes, it is topped with a soil cover. If this cover is designed in a way that it captures and store CO_2, it would not let these emissions go into the atmosphere and would result in ecological use of these wastes. Wastes like C&D and HI ash form a major part of the wastes reaching the landfills. These alkaline wastes can be segregated processed and mixed with soil can result in an effective layer for the landfill for sequestration of CO_2.

2. Materials and Methods

2.1. Sample Collection
Waste samples of C&D, HI Ash and Landfill soil were procured. C&D waste was obtained from IIT Delhi, was crushed, grinded, mixed thoroughly to a homogenous system and sieved through 0.3mm sieve size. HI Ash was procured from Hospital incineration facility. Soil was collected from Okhla Landfill. Samples were oven dried and stored in air tight containers.

2.2. Carbonation Reaction using Batch Reactor
The carbonation reaction was conducted in an acrylic chamber with working volume of 393 liters. The reactor was fitted with two valves for CO_2 injection, a heating rod & a digital thermostat with a PID controller to control temperature, four fans to ensure circulation in the whole chamber and shelves for keeping the samples. CO_2 was passed for 1hr. to stimulate a condition similar to infinite supply.

The humidity was maintained using aqueous solution upto 98%. Carbonation is more rapid at a relative humidity of 50–70%. The temperature was varied from 25°C to 40°C in the intervals of 5°C. The samples were oven dried to ensure that there is no initial moisture content. A 40g sample was used for the experiment. Results were noted for duration of 8hrs, 16hrs, 24 hrs and 48hrs. Fixed water to solids ratio was maintained in all the samples. The post-carbonated samples were oven dried. Samples were then crushed, mixed to a homogenous form, weighed and then stored at room temperature in air tight bags. The dry mass change of the samples was determined and was used to find their respective degree of carbonation.

2.3. Material Characterization
The theoretical extent of carbonation was calculated for the samples using the mineralogical compositions obtained from XRF(X Ray Diffraction Spectrometer) analysis as shown in Table 1 below. The estimation of theoretical extent of sequestration was based on stochiometry and the reactive oxide content in the waste. It was calculated similar to the estimates of Steinour (1959) for concrete & mortars, as follows

$$\%CO_2 = 0.785(\%CaO - 0.56\%CaCO_3 - 0.7\%SO_3) + 1.091(\%MgO - 0.48\%MgCO_3) + 0.71(\%Na_2O - 0.585\%Na_2CO_3) + 0.468(\%K_2O - 0.68\%K_2CO_3) \qquad [1]$$

Table 1: Source and mineral composition of pre-carbonated waste samples

ELEMENTAL COMPOSITION	C&D	HI ASH	LANDFILL SOIL
SiO$_2$	33.6	12.71	54.3

Al$_2$O$_3$	8.78	7.91	11.24
TiO$_2$	0.008	3.14	1.22
Fe$_2$O$_3$	7.43	2.71	5.77
MnO	0.261	0.12	0.16
CaO	41.4	43.1	13.15
MgO	1.61	3.92	1.83
Na$_2$O	0.14	0.81	1.18
K$_2$O	1.38	1.17	3.28
P$_2$O$_5$	0.01	1.16	0.44
SO$_3^{2-}$	1.45	9.7	1.59
Cl$^-$	0.22	2.02	0.4
CaCO$_3$	1.27	6.13	1.97
Theoretical extent of Carbonation	32.55	28.57	11.57

The mass of CaCO3 produced at time (t) taken to be equal to the dry mass gain between pre- and post-carbonated sample is as follows:

$$M_g\ (t) = M_g\ (t) – M_g\ (t= 0) \qquad [2]$$

Where M (t= 0) is the initial dry mass and M (t) is the dry mass after the carbonation reaction. The change in carbonation content (referred as extent of carbonation) can be expressed as CO_2 %(in terms of dry mass):

$$\%\ CO_2\ \text{uptake (t)} = [M_g\ (t)/\ M_g(t=0)] \times 100 \qquad [3]$$

The degree of carbonation (E(t)) was estimated as extent of mass change due to carbonation as a percent of the theoretical extent of carbonation (ThCO2) based on initial composition of the sample:

$$E\ (t) = [M_g\ (t) / [M_g(t=0) \times ThCO_2]] \times 100 \qquad [4]$$

3. Results

3.1. Pre-Carbonation Quantitative Analysis of Samples

The XRF analysis of pre-carbonated samples gave their elemental composition as shown in Table. The theoretical extent of carbonation was calculated using equation[1]. C&D waste shows theoretical CO_2% value of 32.55% while HI Ash has a value of 28.57%. The soil sample that was obtained from a landfill site can be seen to have a theoretical extent value of 11.57%.

3.2. Carbonation of Waste Samples

The carbonation of waste samples was done in the chamber at with a flow of CO_2. At each temperature the progress of carbonation reaction with time was. The final product of carbonation was obtained after 48 hrs. The results for C&D are shown in Figure 1 while those for HI Ash are shown in Figure 2. As shown in Figure 1 a) for 25°C, CO_2 uptake increases with time. In all the graphs, maximum CO_2 uptake can be seen for sample with 0% soil content followed by 25% soil content sample. The maximum value of 10.56% is seen for 0% soil-waste mixture at 30°C.

As subsequently temperature is increased, it is seen that the trend of CO_2 uptake with time varies from the general increase expected with time as seen in the graph for 25°C. At higher temperature i.e. at 35C and 40°C, the post carbonated weight showed that drying was taking place in the reactor. The humidity level was not enough to ensure no drying within the reactor. Similarly graphs were plotted for HI Ash to show the progress of reaction and to compare the different proportions of soil-waste mixture. Again maximum CO_2 uptake is seen for 0% soil content sample. For 30°C again, the maximum value is seen as 9.14% CO_2 uptake for 0% soil.
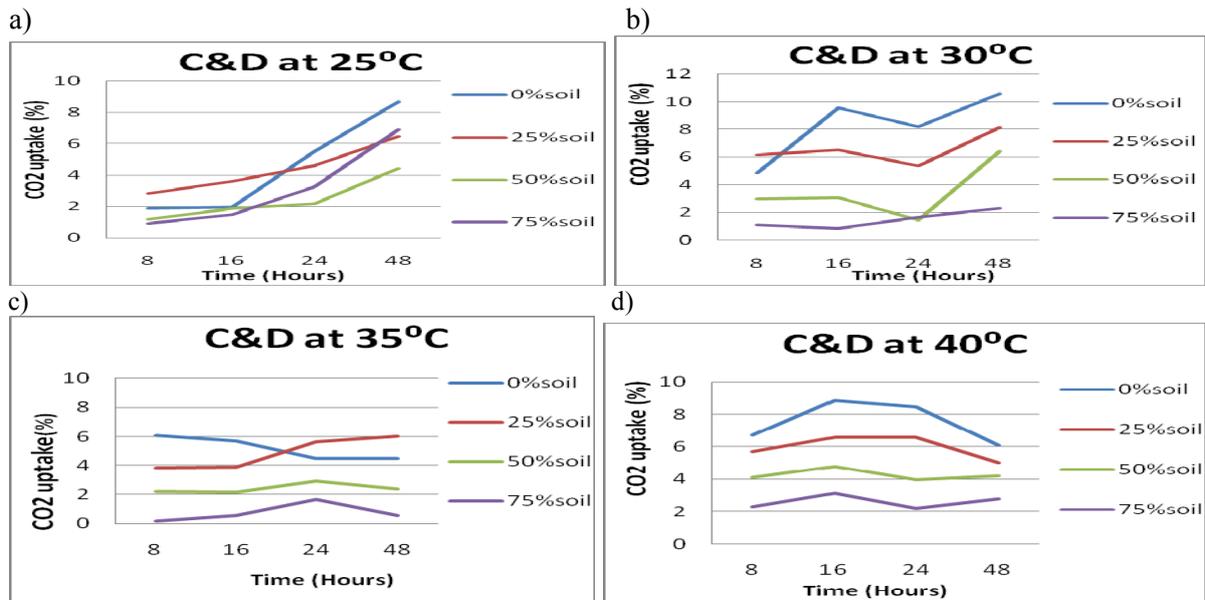
Fig.1: CO_2 uptake of different proportions of soil-C&D waste mixture with time at a) 25°C b) 30°C c) 35°C d) 40°C
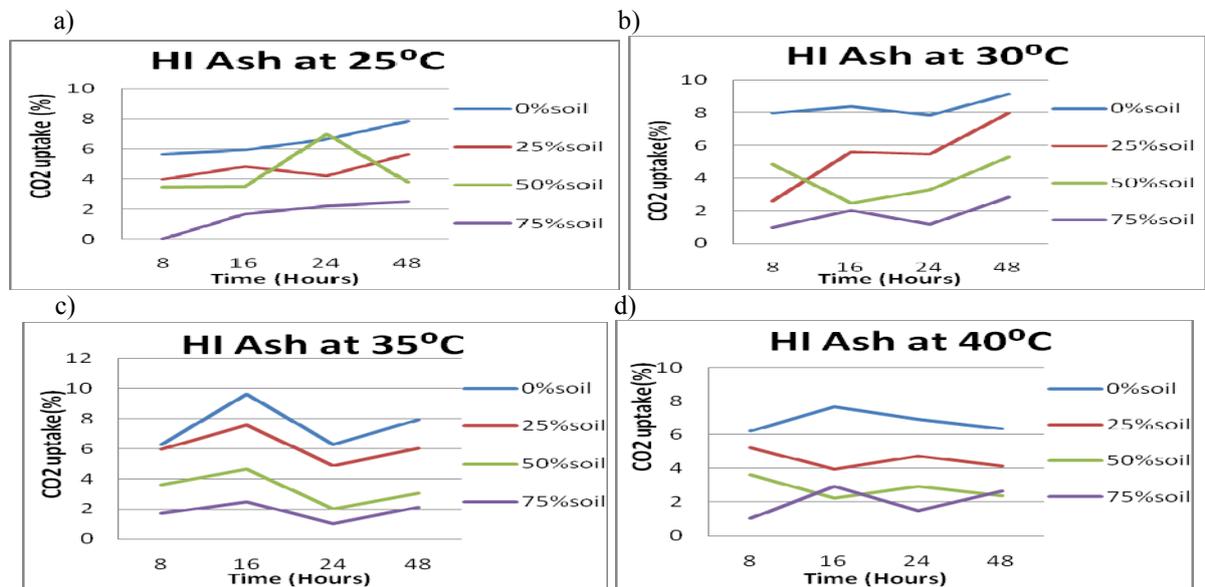

Fig. 2: CO_2 uptake of different proportions of soil-HI Ash mixture with time at a) 25°C b) 30°C c) 35°C d) 40°C

3.3. Determination of Optimum Temperature

It can be seen from Figure 3 that for different proportions of soil-waste mixture, peaking occurs at 30°C for both C&D waste and HI Ash. C&D shows an increase at 40^{0}C after a huge fall at 35^{0}C in CO_2 uptake but the value at 30°C still remains at a maximum. Hence, it can be established here that 30C is the optimum temperature for sequestration of C&D waste and HI Ash.
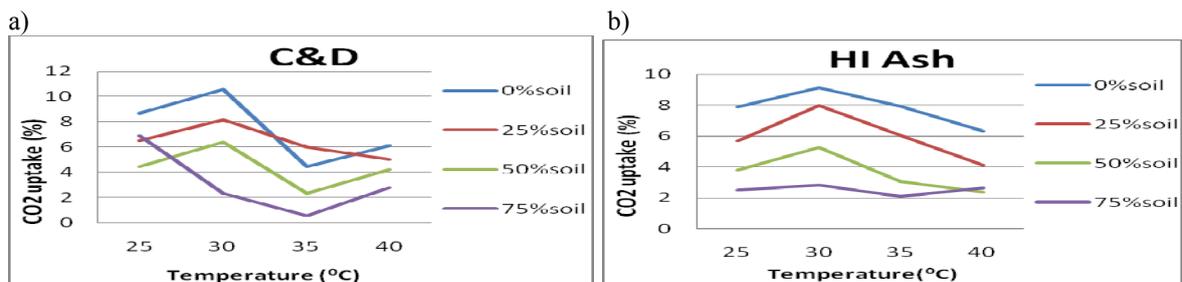

Fig. 3: Variation of final CO_2 uptake of different proportions of soil-waste mixture for a) C&D Waste b) HI Ash

3.4. Degree of carbonation of waste Samples

Degree of carbonation of different proportion of soil-waste mixture at the 4 temperatures can be seen in Figure 4 for C&D and HI Ash. The values are in the range of 5%- 35%. The theoretical extent takes into consideration the reaction of other oxides to form. From Figure 4, it is further reinforced that 0% and 25% soil content in the waste mixture show better carbonation reaction and the degree of carbonation decreases with increasing soil content. Also 30°C can be seen to show maximum degree of carbonation followed by 25°C. The degree of carbonation at 40°C is the least for HI Ash while C&D shows minimum degree of carbonation for 35°C. Thus this analysis validates the effect of increasing temperature in reducing the extent of carbonation reaction.
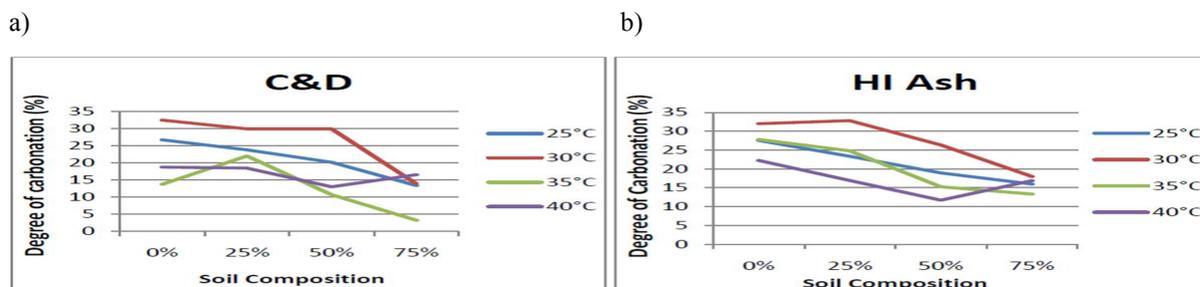
a)   b)

Fig. 4: Degree of carbonation with soil composition at different temperatures for a) C&D Waste b) HI Ash

4. Summary & Conclusions

This research provided an insight into the CO_2 mineral sequestration of alkaline wastes under different conditions of carbonation reaction such as temperature and soil-waste proportion. Maximum CO_2 uptake was determined to be 10.56% for C&D waste and 9.14% for HI Ash at 0% soil content in the soil-waste mixture at 30°C. C&D waste achieved a higher CO_2 uptake than HI Ash at all proportions of soil content and all temperatures. Thus C&D can be considered better suited for use as a cover in landfills than HI Ash. Maximum CO_2 uptake and degree of carbonation was obtained for a soil-waste mixture of 0% and 25% soil content. Thus a pure waste or a 25% soil content waste can be suggested as a possible cover for landfills. Only a small % of theoretical extent of carbonation(in the range of 5-35%) was realized in the carbonation reaction thus showing the large gap between the theoretically estimated and the experimentally calculated value of CO_2 uptake. The research helped establish an optimum temperature for the carbonation reaction at which maximum CO_2 uptake was achieved. The optimum temperature for C&D waste and HI Ash was determined as 30°C.

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