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Mineral Carbon Sequestration by Alkaline Waste and Its Use in Landfill

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ABSTRACT
The Municipal Corporation of Delhi (MCD) is among the largest municipal bodies in the world. It provides its civic services about 18 million people (estimated population of Delhi). Environmental impacts of municipal solid waste (MSW) management like emissions of greenhouse gases (GHGs) have been greatly reduced by Technological advancements, environmental regulations, and emphasis on resource conservation and recovery. The aim of this work was to quantify the volume of CO_2 emitted from MSW Landfill and sequester it with a view to reduce greenhouse gas emissions. The alkaline waste like construction and demolition (C&D) waste or Hospital Incineration (HI) waste has ability to capture carbon dioxide. The theoretical carbon dioxide sequestration potential of C&D waste and HI ash is 32.55% and 28.57% respectively through various models like Default methodology and Land GEM model.
***Key Words*: Municipal Solid Waste, Carbon Sequestration, Greenhouse Gases, Default methodology, Land GEM model**

I. INTRODUCTION

India is the second most populated country in the world followed by China. The population growth of India is increasing in very fast rate and it is believed that it will be at top position in near future. There is high increase of urbanization and industrialization in all over world. It is estimated that by the year 2050 out of total population the urban population accounts 86% in developed countries and 64% in developing countries respectively (Tacoli, 2012; UNPD, 2012).

The population growth, urbanization and industrialization have led to number of land use and infrastructural challenges that include higher rate of MSW generation and challenges with its management (Singh et al, 2014). It was estimated that in 1990 about 1.3 billion MT of MSW was generated globally while at present time nearly after two decade, the yearly production of solid waste is about 1.6 billion MT. The cities, which have more than 100,000 populations, contribute to more than 72 per cent of the total MSW (Da Zhu P. et al., 2008). It is the general believe that the rate of waste generation is an index of socio-economic development of the country. The rate of MSW generation is more prominent in the developing countries because of their high rate of unplanned urbanization. According to Central Pollution Control Board (CPCB, 2005), the annual MSW generation in India ranges between 40-55 million tons per year and this Fig. could be 270 million tons in 2047 (Fig. 1).

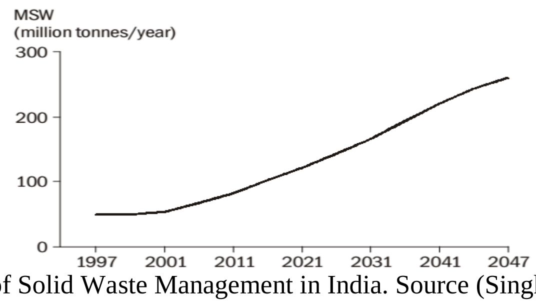

Fig.1. Projected trend of Solid Waste Management in India. Source (Singhal and Pandey, 2001)

The MSW is collected, segregated and finally dumped into the landfill. The municipal solid waste, which goes to landfill, has high amount of food and other biodegradable constituents. In Indian MSW, which goes to landfill, has high amount of food and other biodegradable constituents (approximately 40-60%). The other waste constituents are ash & fine earth (30–40%), paper (3–

6%) and plastic, glass and metals (each less than 1%). During the course of time there is many bio-chemical reaction occurs in landfill through which this waste has been degraded (Sharholy et al., 2006; Shekdar, 1992; Thitame et al, 2010). The construction industry generates a significant amount of wastes from such as the land excavations, clearance of land, site work, building work, and demolition which lead to the generation of a significant amount of construction and demolition "C&D" waste (Gupta et al., 2011; Shen et. al., 2004; Tam et. al., 2008). During the course of time there are many chemical reactions occur in landfill through which the MSW is degraded. This degradation leads to generation of mainly methane and Carbon dioxide (CO_2). The methane gas released is extracted and used up into energy production where it is converted into CO_2. So that CO_2 is, the major gas released from landfill site. The Table 1, shown clearly depicted the relation among urban population, per capita MSW generation and per capita carbon dioxide emission (World fact sheet, 2001, World Bank, 2003, CDIAC,).

Table 1. Increase in Urban Population of India

Years	Urban population (% in total)	GDP per capita (%)	Municipal solid waste generation per capita (kg day^{-1})	Per capita Carbon dioxide emission (in metric tons)
2007	12.28	5.3	0.75	1.3726
2010	17.35	6.0	0.79	1.6404
2030	32.43	7.0	0.97	3 to 5

The first objective of the present study was to characterization of different quality control parameters and assessment of CO_2 emission from municipal solid wastes. Second objective is estimate the alkaline waste alkaline waste from construction and demolition (C&D) waste or Hospital Incineration (HI) waste.

1.1 Literature Review

Carbon sequestration refers to different methods that transfer atmospheric CO_2 into long-lived pools and keep it stored permanently so that it is not re-emitted back to atmosphere immediately (Lal et al. 2003). There are four type of process for carbon sequestration namely terrestrial carbon sequestration geological carbon sequestration, ocean sequestration and mineral sequestration. Mineral carbonation process is one of the best methods for carbon dioxide removal because it results permanent storage of carbon dioxide as mineral carbonate without any external energy inputs. Mineral carbon sequestration using alkaline waste is a new technology. The mineral carbon sequestration process has achieved more attention due to its exothermic reaction and raw material abundance. This carbonation process is thermodynamically favored and form lower energy state carbonates (Herzog, 2002). This method is one of the safest methods for CO_2 sequestration in nature. This process involves the bringing in contact high conc. of CO_2 with metal oxide, resulting in formation of stable carbonates for example reaction of CO_2 with Ca or Mg form a final stable product such as $CaCO_3$ and $MgCO_3$ (Lackner et al. 2002, Fauth et al. 2005).Carbonation reactions have been investigated widely in alkaline waste, which shows that the alkaline waste is a feasible option to decrease the CO_2 emission in the atmosphere (Huijgen et al. 2003; Bertos et al. 2004).Alkaline waste includes C&D waste, fly ash, HI waste etc.

Construction industry is blooming in India so that quantity of C&D waste is also growing. The main constituents of C&D waste are CaO, MgO, SiO_2, Al_2O_3 and Fe_2O_3 (Pappu et al. 2007). Various studies have been conducted so far shows that C&D waste have high potential in CO_2 capture (Gupta et al. 2011). The reactions mechanism for carbonation reaction can be shown simply reaction of alkaline waste with CO_2 as given below.

$$CO_{2(g)} + H_2O \rightarrow 2H^+ + CO_3^{2-}{}_{(aq)} \quad \text{eq 1}$$

$$CaSiO_{3(s)} + 2H^+ \rightarrow Ca^{2+}_{(aq)} + SiO_{2\,(s)} + H_2O_{(l)} \quad \text{eq 1}$$

$$Ca^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow CaCO_{3(s)} \quad \text{eq 1}$$

$$CaSiO_{3\,(s)} + CO_{2\,(g)} \rightarrow CaCO_{3(s)} + SiO_2 + 90\text{kJ mol}^{-1}CO_2 \quad \text{eq 1}$$

$$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2 + 89\text{kJ mol}^{-1} + CO_2 \quad \text{eq 1}$$

$$(Ca,Mg)SiO_{3(s)} + CO_{2(g)} \rightarrow (Ca,Mg)CO_{3(s)} + SiO_{2(s)} \quad \text{eq 1}$$

These reactions are exothermic in nature and favored at low temperature. The carbonate formation occurs spontaneously in nature due to natural CO_2 rich fluids percolation into mineral deposits. The carbonates formed are stable and not likely to release the bound CO_2 again into the atmosphere.

II. METHODOLOGY

MSW represent the largest mass of solid materials generated by humanity. As the population of the world is keeping on escalating, the MSW is also keep on rising. This generated MSW is goes either into the open dumping site or in the landfill. In the developing countries these organically rich solid waste generally disposed into open dump; only small fraction is processed by composting or vermi composting. The first step in MSW management is the segregation of waste, which can be categorized into biodegradable waste and non-biodegradable waste. Before the final disposal of MSW into landfill sites or dump, major part of MSW is recycled, conducted by rag pickers. The Figure 2 given below describes the MSW management.

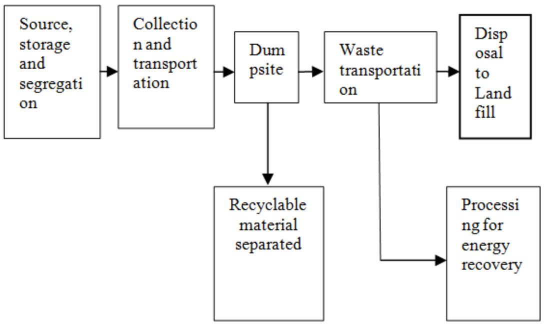

Figure 2. Flow chart of MSW management

Due to course of time the developing countries like India moves from open dump to sanitary landfill or bioreactor landfill. This bioreactor landfill contain surface water drainage system, environmental monitoring system, leachate collection and treatment system bottom liners, daily covers, and landfill gas collection system**.**

2.1 Landfill Gas Generation

The MSW that goes to landfill has high amount of food and other biodegradable constituents. During the course of time there are many chemical reactions occur in landfill through which the MSW is degraded as the time passes. This waste generation phase include five more or less sequential phase from Phase-I to Phase-V. Phase-I is aerobic decomposition phase in which CO2 gas is generated. The oxygen content in landfill decreases with time and anaerobic condition developed that leads to the onset of Phase-II i.e. transition phase. Due to course of time oxygen content is very less or absent within the landfill hence landfill reaction is strictly anaerobic. This phase is known as Phase-III or anaerobic phase. At offset of Phase-III, methanogen became active and methane gas emission becomes predominant (phase IV). The Phase V of the landfill is known as maturation phase. In maturation phase the biodegradable nutrient is very less so that the landfill gas emission is quite low. Landfill gas composition is presented in Table 2.

Table 2. Percentage composition of landfill gas

Gases	Methane	Carbon dioxide	Nitrogen	Oxygen	Ammonia	NMOCs*	Sulfides
Percentage content	45–60	40-60	2-5	0.1-1	0.1-1	0.01-0.6	0-1

NMOCs * Non-methane organic compounds

2.2 Delhi Landfill Sites

In Delhi, India there is three-landfill site named Okhla, Ghazipur and Bhalaswa. These landfill sites are clearly shown in the Figure 3. Theses landfills are the sink for the MSW collected from whole Delhi. The description of landfill site with respect to starting year, locality, area covered and waste received until this time, is given in Table 3.

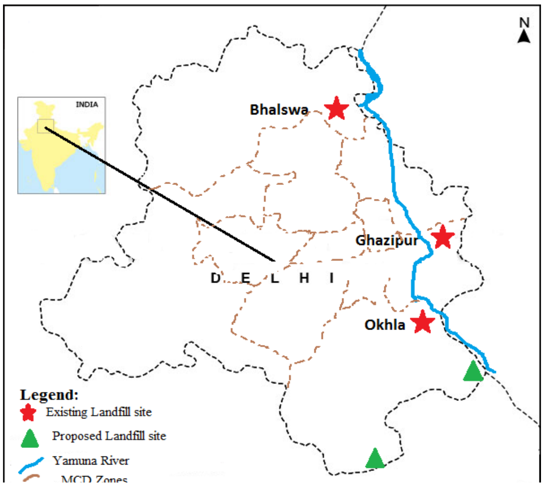

Figure 3. Location of existing landfill site in Delhi.

The landfills present in Delhi, India are well maintained as per Indian scenario. The waste acceptance for all the three landfills is given in Table 4. The annual waste acceptance and the structural features of sites affect the landfill gas emission. The landfill area of Gazipur Landfill (29.16 Ha) is higher than Bhalswa Landfill (21.06 Ha) and Okhla Landfill (16.2 Ha). Hence, waste acceptance is high in Gazipur Landfill followed by Bhalswa Landfill and Okhla Landfill.

Table 3. Existing Landfill sites in Delhi

SN	Features	Ghazipur	Bhalswa	Okhla
1	Location	28 370 22.400 N, 77 190 25.700 E (East Delhi)	28 44027.1600 N, 77 90 27.9200 E (North Delhi)	28300420 0 N, 77 160 5900 E (South Delhi)
2	Started year	1984	1992	1996
3	Year of closure	2012	2010	2011
4	Area (Ha)	29.16	21.06	16.2
5	Waste Received	2000 TPD*	2200 TPD*	1200 TPD*
6	Waste collected from the zone	Shahdara (North), Sadar, Paharganj and NDMC area	Civil Line, Karol Bagh, Rohini, West Najagarh	Central and South, Najafgarh and Cantonment area
7	Annual precipitation (mm/year)	706	706	706
8	Density (tones/m3)	1.2	1.2	1.2
9	Technology used	Aerobic windrow Composting	Aerobic windrow composting	Aerobic windrow composting

* TPD: Tones per Day.

Table 4 Quantity of SW reaching Delhi landfill site

	Year-wise	Waste Acceptance (in tons)		
		Bhalswa Landfill	Okhla Landfill	Gazipur Landfill
1.	2002-03	69072	27216	1691083
2.	2003-04	77009	31180	1907599
3.	2004-05	82773	30004	1929465
4.	2005-06	60236	35249	2061538
5.	2006-07	54566	33736	1903583
6	2007-08	60674	30836	1524059
7	2008-09	69617	33807	1659741
8	2009-10	70134	37379	1845896
9	2010-11	58711	40554	2072873
10	2011-12	49366	41896	2080736

III. RESULT AND DISCUSSION

3.1 Methods for GHG Quantification

The various researchers have constantly done the landfill gas estimation across the globe. There are various landfill model for estimating gas such as biochemical model, empirical model, Land GEM model and stoichiometric models. According to IPCC 1996 in Indian Scenario, Default method (DM) and first order decay (FOD) methods are recommended for LFG estimation.

A. Default methodology (DM)

It is an empirical model with a number of empirical constant. These empirical constant depend upon waste compositions and its management. Total carbon dioxide yield for the waste dumped into the landfill can be computed by using equation 1.

Emission = $(MSW_T \times MSWF)_X$ MCF x DOC x DOC_F x F x (16/12-R) x (1-OX) Eq. 1

Where, MSW_T is the total MSW reaching in the year 20011-12, i.e. 2080736 tones, 49366 tons and 41896 tons for Gazipur Landfill, Bhalswa Landfill and Okhla Landfill respectively. MCF (methane correction factor) is taken as 0.4 for unmanaged landfill site having depth < 5 m, and based on waste composition DOC (Degradable organic carbon) value for Delhi is taken as 0.15. Default value for dissimilated organic fraction (DOCF) and fraction of methane in LFG (F) is 77% and 50%, respectively. R (Recovered methane) and OX (Oxidation factor) is assumed zero for Delhi.

Total carbon dioxide gas generation is calculated for Gazipur Landfill, Bhalswa Landfill and Okhla Landfill are42934.81 tones, 49366 tones and 41896tons respectively in the year 20011-12. The waste acceptance in the time span of 10 years from 2002 to 2012 for Gazipur Landfill, Bhalswa Landfill and Okhla Landfill are 18676573 tones, 652158 tones and 341857 tonsrespectively. The total carbon dioxide gas generated from 2002 to 2012 for Gazipur Landfill, Bhalswa Landfill and Okhla Landfill are 385380.5 tones, 13456.91 tones and 7054.025 tonsrespectively. The carbon dioxide gas emission for all three landfill is summarized in the Table 5. **Table 5.**Estimation of CO_2 gas emission from landfill by Default Method

S.N.	Year	CO_2 gas emission (in tons) by Default Method		
		Gazipur Landfill	**Bhalswa Landfill**	**Okhla Landfill**
1.	2002-03	34894.54	1425.261	561.5867
2.	2003-04	39362.22	1589.037	643.3816
3.	2004-05	39813.41	1707.974	619.1155
4.	2005-06	42538.67	1242.936	727.3431
5.	2006-07	39279.35	1125.938	696.1232
6	2007-08	31448.09	1251.974	636.2833
7	2008-09	34247.81	1436.507	697.5882
8	2009-10	38089.02	1447.175	771.2944
9	2010-11	42772.56	1211.468	836.8087

B. Land gem model

The estimation of landfill gases (LFG) is done through model stipulation. Here the Land GEM model is used to calculate the Landfill gas generation from the landfill. It is the automated tool developed by American Environmental Protection Agency (US E.P.A) to quantify landfill gases. This model is based on simple degradation equation. The model determines the mass of methane generated with the help of methane generation capacity and the mass of waste deposited. The Land GEM model can be described as

$$Q_{CH_4} = \Sigma_{i=1}^{n} \Sigma_{j=0.1}^{1} kL_0 \frac{(M_j)}{10} (e^{-kt}) \text{Eq. 2}$$

Where, i is the time elapsed in unit of year; n is the difference between final and initial year of waste acceptance, k is the methane generation constant (yr^{-1}) and L_0 represents the methane generation potential in unit (Mg/m^3). In the equationj is the 0.1 year time increment;M_i the mass of degradable refuse waste at the initial time and $t_{i,j}$is the age of the j^{th} section of waste Mi accepted in the i^{th} year (decimal years). This model depends upon variables like Historic and projected waste disposal rates, Methane decay rate,Methane generation potential and Collection efficiency. The carbon dioxide gas estimation through Land GEM model is calculated (Table 6).

The input data used for the Land Gem model are methane generation rate (k), methane content and potential methane generation capacity (L_0). The methane generation rate (k) and potential methane generation capacity (L_0) for the bioreactor landfill are 0.050 $year^{-1}$ and 170 m^3/Mg respectively. The methane content is 50% by volume. Through this model the total landfill gas emission, methane gas emission and carbon dioxide gas emission have been estimated as in Figure 4 given below. Here in this study the gas estimation is done for all the three landfills in Delhi through Land GEM model as shown in Table 6.

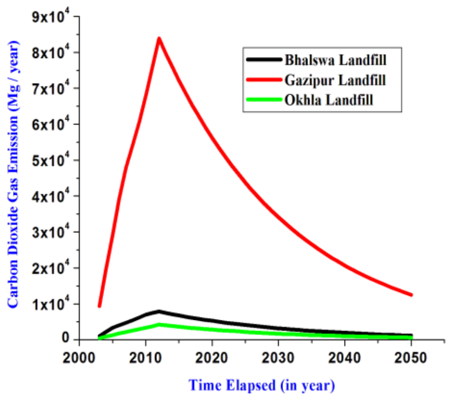

Figure 4. Annual carbon dioxide gas emission from landfill

The daily waste acceptance of Bhalswa landfill is comparatively more than Gazipur and Okhla landfill. Hence, the gas emission from the Bhalswa landfill is also higher than other landfills.

Table 6. Estimation of CO_2 gas emission from landfill by Land Gem

S.N.	Year	CO_2 gas emission (in m^3/yr.) by Land GEM Model		
		Gazipur Landfill	Bhalswa Landfill	Okhla Landfill
1	2002-03	12780000	521900	205600
2	2003-04	26570000	1078000	431200
3	2004-05	39850000	1651000	636900
4	2005-06	53490000	2026000	872200
5	2006-07	65260000	2339000	1085000
6	2007-08	73590000	2684000	1265000
7	2008-09	82550000	3079000	1458000
8	2009-10	92470000	3459000	1670000
9	2010-11	103600000	3734000	1895000
10	2011-12	114300000	3925000	2119000

3.2 Sequestration Of Carbon Dioxide Gas

The landfill generally accepts the waste for 20 years and it is assumed that it can be utilized for LFG production up to 40 years. The CO_2 production from landfill is continued even after closure of landfill. The alkaline waste is required to sequester CO_2, as a daily cover of each cell within the landfill before its closure. The alkaline waste can also be provided as an intermediate cover between or around the LFG collection wells so that all the CO_2 is captured within the landfill itself .Here in the study it is assumed that 50% of gets captured in one layer and the rest gets transferred to the above successive layer.

The CO_2 produced till entire life span from landfill is calculated and found 2,779,568 tones. The total C&D waste needed for whole life span of landfill is 8,539,379 tones and HI waste needed is 9,728,974 tones. This shows C&D waste is more useful for carbon sequestration in comparison to HI waste. Requirement of alkaline waste corresponding to CO_2 emission is shown in Figure 5.

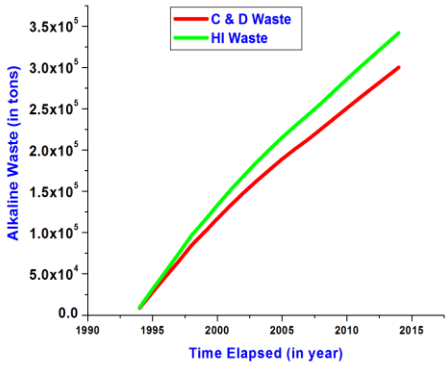

Figure 5. Alkaline waste required for conventional landfill

IV. CONCLUSION

Capturing and separation of CO_2 from landfill can be achieved through continued research, development and demonstration. This research is being performed to abate global climate change, which is consequence of GHG emission (IPCC, 2007). The mineral carbon sequestration is only known form of permanent solution for carbon storage in a single step. Silicate of calcium and magnesium minerals is often used for mineral carbonation but it requires energy intensive pretreatment to achieve optimized carbonation conversion and acceptable kinetics. Hence, certain alkaline wastes are used as an alternative source of mineral alkalinity. These alkalinewastes have their specific sets of advantages and disadvantages in term of CO_2 sequestration. Therefore, it is difficult to compare them for mineral CO_2 sequestration. Here in this paper two type of waste is considered namely C&D waste (CO_2 sequestration potential 32.55%) and HI waste (CO_2 sequestration potential 28.57%) (Gupta et al. 2011). Due to high CO_2 sequestration potential, C&D waste required is less in quantity in comparison to HI waste. These waste must have undergo through size reduction that increases the rate of carbonation reaction.

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