

CO₂ Sequestration Potential of Construction and Demolition Alkaline Waste Material in Indian Perspective

G.Anjali, M.Bhavya, and N.Arvind Kumar

Abstract—In order to avoid the potentially devastating consequences of global warming and climate change, the carbon dioxide “CO₂” emissions caused due to anthropogenic activities must be reduced considerably. This paper presents the first study examining the feasibility of carbon sequestration in construction and demolition “C&D” waste. Experiments were carried out in a self fabricated Batch Reactor at 40°C, relative humidity of 50-70%, and flow rate of CO₂ at 10L/min for 1 hour for water-to-solids ratio of 0.2 to 1.2. The effect of surface area was found by comparing the theoretical extent of carbonation of two different sieve sizes (0.3mm and 2.36mm) of C&D waste. A 38.44% of the theoretical extent of carbonation equating to 4% CO₂ sequestration extent was obtained for C&D waste sample for 0.3mm sieve size. Qualitative, quantitative and morphological analyses were done to validate carbonate formation using X-ray diffraction “X.R.D.,” thermal gravimetric analysis “T.G.A.,” “X-Ray Fluorescence Spectroscopy “X.R.F.,” and scanning electron microscopy “S.E.M”.

Keywords—Alkaline waste, construction and demolition waste, CO₂ sequestration, mineral carbonation.

I. INTRODUCTION

INCREASED public awareness of the threats posed by global warming has led to an immediate concern over the adverse impacts posed by various anthropogenic emissions in the atmosphere. Various carbon sequestration technologies developed are today focusing on mitigation of these emissions. Indian economy is growing at a rate of 9% per annum, accounting for a significant amount of emissions of the green house gases by the use of fossil fuels. India's agriculture and natural resources will be severely hit by the adverse impact of climate change according to the Intergovernmental Panel on Climate Change, “I.P.C.C.” [1]. The annual carbon dioxide “CO₂” emissions from large point sources in India for the year 2006 was estimated to be 721 Metric tonne “M.T.” CO₂, roughly half of total emissions of 1343 MT in 2004 [2].

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To avoid the adverse effect of climate change caused by increased anthropogenic emission into the atmosphere, carbon capture and storage technology needs to be explored. Carbon dioxide sequestration efforts have so far focused on the storage of CO₂ in natural reservoirs such as the oceans, geologic formations, and terrestrial biosphere and solid storage by reaction of CO₂ with metal oxides to produce stable carbonates [3], [4]. Carbon sequestration by mineral carbonation involves reaction of naturally occurring mineral with CO₂ to form a safe and stable mineral carbonate product.

Mineral carbonation reactions results in a stable end product, namely the carbonate, which encouraged us to investigate and carry out future research at a laboratory scale. Natural carbonation reaction is a very slow process and its application on a large scale is not fully understood. Carbonation reaction by using alkaline waste material like coal fly ash, municipal solid waste incinerator ash, and steel slag have been investigated in preliminary experiments with comparable results [5], [6], [7], [8]. Mineral carbonation studies in alkaline waste material have also been carried out in aqueous batch reactor and also at elevated temperature and pressure conditions [5], [8].

The alkaline waste material acts as a potential source for capturing carbon dioxide. High surface area, fined grained, readily available, generated at point source, and rich source of calcium and magnesium, are few properties which makes them a potential source for mineral sequestration. Though most of the carbonation reaction has been carried out on Mg silicates, CaO carbonation reactions are thermodynamically more favourable under ambient conditions [4].

Waste is defined as any material by-product of human and industrial activity that has no residual value [9]. About 50 million tons of municipal solid wastes “M.S.W” are generated in India every year [10]. The construction industry consumes a large amount of resources. Construction process involves activities like clearance of land, site work, land excavations, building work, and demolition waste. This results in the generation of tremendous amount of construction and demolition “C&D.” waste [11], [12], [13]. Two types of waste are generated in by a construction industry, namely process waste and demolition waste. C&D waste comprises of a mixture of inert, inorganic and organic material like debris, clay, stone, gravel, tiles, blocks, concrete, cementitious material, timber, steel, aggregates and sand. As these materials are acquired naturally, their continuous exploitation will have

a devastating effect on the environment. Emission of carbon monoxide, particulate matter, nitrogen dioxide, sulphur dioxide, decomposition of calcium carbonate and lime, forms part of the manufacturing process.

Reference [14] shows that India accounts for 14.5 MT of waste generated by the construction sector. Some amount of this construction waste is being recycled as building material. Marble industries alone accounts for 6 metric tonne MT of the waste arising from the marble manufacturing process. About 70% of this is disposed off locally, accounting for an immediate environmental concern [15]. This waste poses a much greater concern with respect to the volume generated. Reference [16] stated that approximately 50-70% of it is recycled and reused in construction process.

C&D waste generation accounts for 40% of total waste generated globally. United States accounted for 136 MT of C&D debris for the year 1996 [17]. C&D waste generation for United Kingdom in late nineties accounted for around 70 MT [18]. In Australia, C&D waste accounted for approximately 16-40% of the total waste generated in the country in the mid nineties [19]. For Hong Kong, 20MT of C&D waste was generated in 2004 [20].

The overall goal of this paper is to investigate the use of solid alkaline industrial C&D waste to sequester CO₂. It aims to focus on the mineral sequestration of carbon dioxide in alkaline industrial waste through the process of mineral carbonation. The paper focuses on the demonstration of the feasibility of mineral carbonation of C&D waste products and shows its viability as a potential sequestration technology.

II. MATERIALS AND METHODS

A series of batch experiments were conducted on C&D waste, collected from a construction waste pile site at I.I.T Delhi. The reactions were carried out in a self fabricated batch reactor, under varying conditions of w/s ratio. Temperature, humidity and CO₂ gas flow conditions were standardized prior to the experimentation. Various analytical tools were used to support and demonstrate the feasibility of mineral carbonation in C&D waste product.

A. Sample Collection

The C&D waste was grinded and mixed to a fairly homogenous system. The grinded waste was then sieved through a 2.36mm and a 0.3mm sieve to obtain two samples of C&D, represented as C&D (L) "large" and C&D(S) "small" respectively. The samples were dried and stored at room temperature in air tight containers

B. Fabrication of Batch Reactor

The batch reactor for carbonation reaction as shown in Fig 1 below was first fabricated. The reactor was a rectangular acrylic chamber of dimensions 109.73 cm × 73.15 cm × 60.96 cm that provided a working volume of 393litres. A number of fittings and settings were done to create the suitable conditions for reaction.

The chamber allowed inflow of CO₂ through two valves fitted on one side of the reactor wall. The CO₂ was passed using a CO₂ cylinder with a regulator. A rotameter was fitted in the flow path to regulate the gas flow.

The reactor was also fitted with a heating rod & a digital thermostat with a P.I.D controller to control temperature, four fans to ensure circulation in the whole chamber and shelves for keeping the samples.

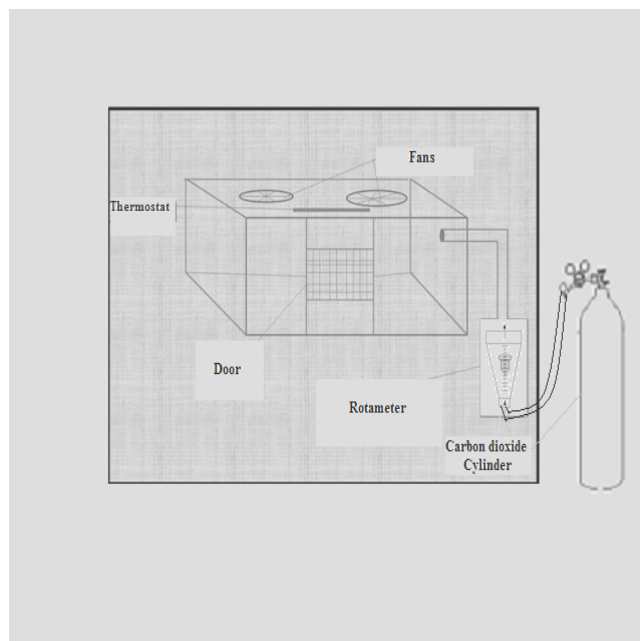


Fig. 1 Batch reactor for carbonation reaction

C. Carbonation Reaction

The temperature in the reactor was set to 40°C and humidity was maintained using aqueous solution of K₂SO₄ (111g/L) which has an Humidity Fixed Point "H.F.P." of 98 [21]. A 2.5litre solution helped effectively maintain the humidity in the range of 50-70% as determined by an indoor air quality monitor. Two troughs containing the solution were placed in the chamber and were regularly renewed to account for lost vapours. CO₂ was passed into the chamber for 1 hour, at a flow of 10L/min.

The samples were oven dried at 100°C to ensure that there is no initial moisture content. Samples, weighed to 50grams, were placed in steel containers and combined with distilled water to obtain definite w/s ratio. Six different ratios by mass, 0.2 to 1.2 in increments of 0.2 were obtained for the carbonation reaction. The samples were then kept in the chamber with the conditions set for the carbonation reaction. The chamber was closed and the reaction was allowed to continue for 16hr.

The post-carbonated samples were oven dried at 100°C for 2hr, crushed, mixed to a homogenous form, weighed and then stored at room temperature in air tight bags. The carbonation reaction results were noted for duration of 4hr, 8hr, 12hr and 16hr for different w/s ratio. The dry mass change of the

samples was determined and was used to find their respective degree of carbonation. Results were further confirmed with various material and morphological characterization methods as discussed below.

D. Material Characterization

The XRF analysis of pre-carbonated samples gave their elemental composition. The theoretical extent of carbonation (θ) was then obtained by plugging in the % of various constituent compounds as in (1). The estimation of theoretical extent of carbonation was based on stoichiometry and the reactive oxide content in the waste. The theoretical extent gives the percentage dry mass of sample reacted, that can be expected to be converted into carbonate on reaction with CO_2 , thus giving the extent or potential of the waste to sequester CO_2 . It was calculated (as a percent of initial dry mass of sample), similar to the estimate for concrete & mortars[22], as follows:

$$\theta = 0.785(\% \text{CaO} - 0.7\% \text{SO}_3 - 0.56\% \text{CaCO}_3) + 0.71\% \text{Na}_2\text{O} + 1.091\% \text{MgO} + 0.468(\% \text{K}_2\text{O} - 0.632\% \text{KCl}). \quad (1)$$

In the above equation, the stoichiometric factors take into account the assumption that all the oxides of Na, Ca and Mg convert to carbonates. Presence of initial CaCO_3 , CaO in bounded form of CaSO_4 and K_2O in bounded form of KCl are discounted for.

The above formula is based on (2), (3), (4) & (5), as suggested below:



Table 1 shows the elemental composition and the theoretical extent of carbonation. C&D(L) and C&D(S) have different theoretical carbonation extents due to chemical composition variation due to non homogeneity. Thus based on stoichiometry and the elemental composition of C&D waste material, the total sequestration potential was calculated to be 14.41% and 23.62% for C&D(L) & C&D(S) respectively. Every 1kg of C&D waste sample has the potential to capture 0.144kg and 0.236kg of CO_2 .

CaO was the main oxide in the sample (as per XRF results in Table1), and the conditions of reaction were set for calcite production. We assume that the main product of carbonation reaction was CaCO_3 . Since the theoretical extent of CO_2 sequestration potential of C&D(S) waste sample was relatively higher than C&D(L), it was used for all the analysis.

The mass of CaCO_3 produced at time (t) taken to be equal to the dry mass gain between pre- and post-carbonated sample is as shown in (6) below:

$$M_g(t) = M(t) - M(t=0) \quad (6)$$

Where $M(t=0)$ is the initial dry mass and $M(t)$ is the dry mass after the carbonation reaction. The change in carbonate content (referred as extent of carbonation) can be expressed as ε (in terms of dry mass %) as shown in (7) below.

$$\varepsilon = [M_g(t)/M(t=0)] \times 100 \quad (7)$$

TABLE I
MINERAL COMPOSITION OF PRE CARBONATED WASTE SAMPLES

Elemental Composition	Waste Sample	
	C&D(L)	C&D(S)
SiO_2	57.68	43.28
Al_2O_3	7.71	7.24
TiO_2	0.56	0.55
Fe_2O_3	2.31	2.33
MnO	0.106	0.102
CaO	18.47	31.77
MgO	1.54	1.15
Na_2O	0.56	0.31
K_2O	1.02	0.88
P_2O_5	0.12	0.22
SO_3^{2-}	0.88	1.12
Cl^-	0.008	0.01
CaCO_3	4.92	5.89
Theoretical extent of Carbonation	14.41	23.62

Thermal gravimetric analysis (TGA) was conducted for the samples to verify the observed mass change was due to CO_2 sequestration. A sample subset was heated in a nitrogen atmosphere till 1000°C at $20^\circ\text{C}/\text{minute}$. TGA results gave the amount of change in weight as a function of temperature. Carbonate decomposition occurs in the range of $500\text{--}850^\circ\text{C}$. The change in carbonate content was obtained by comparing the results of pre- and post-carbonation samples. The change in total carbonate content is assumed to be solely a result of CO_2 sequestration.

To verify and confirm the reaction products and assess presence and abundance of specially calcite, qualitative analysis of mineralogical composition of pre- and post carbonated samples was carried out by X-ray diffraction (XRD, powder method) using a PANalytical PW 3040/60 X'Pert PRO diffractometer. The working conditions were $\text{K}\alpha$ radiation ($\lambda=1.540798 \text{ \AA}$), 40kV and 30mA. Specimens were scanned from $20\text{--}70^\circ 2\theta$, with a step-size of $0.02^\circ/\text{min}$.

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 (θ) based on initial composition of the sample as shown below in (8).

$$E(t) = M_g(t)/[M(t=0) \times \theta] \quad (8)$$

The degree of carbonation was a factor used to evaluate the progress of carbonation in the reactor and compare between

the reactions shown by the two different particle sizes of 0.3mm and 2.36mm.

In order to observe the microstructure and carbonate precipitation, Scanning Electron Microscopy "S.E.M" analysis was performed at 20kV and 10K magnification using an Evo 50 Zeiss instrument. Energy-dispersive X-ray spectroscopy "E.D.S." was conducted on one of the samples to show the carbonate content of product precipitate

III. RESULTS AND DISCUSSION

Quantitative and qualitative analytical methods of XRD, XRF and SEM were performed on the C&D(S) samples to evaluate the CO₂ sequestration potential of C&D waste. Preliminary to carbonation the process of standardization was performed. The reaction required standardization towards humidity control, temperature of reaction, and drying period of post-carbonated samples for obtaining the dry weight.

The experiments were conducted in the months of June-July, so there were temperature fluctuations towards the higher side as the atmospheric temperature rose. Thus the working temperature was standardized to 40°C, 2°C above the average external temperature of 38°C.

A. Elemental and Mineral Characterization of Pre-carbonated C&D waste

The elemental composition of the pre-carbonated C&D(S) waste sample was determined for the present study, which is listed in Table 1 above. It represents the percentage of various element oxides present in the given sample. The pre-carbonated C&D(S) sample, in the unreacted form, had comparably high percentage of CaO with moderate to low percentages of other metal oxides like K, Na and Mg.

XRD Analysis performed on samples, detected various mineral phases like calcite, anhydrite and quartz. The presence of calcite in pre-carbonated samples indicated that the sample has undergone some degree of carbonation, prior to its subjection to batch reactor.

B. Carbonation of C&D Waste

Once standardization was achieved, the carbonation of C&D(S) waste samples (0.3mm sieve size) was conducted at the standardization-concluded working conditions. The results have been shown in fig 3 in the form of Degree of Carbonation v/s Time graphs for different w/s ratio (0.2 to 1.2). The maximum degree of carbonation was obtained for 0.4 w/s ratio. Thus 0.4 is the optimum ratio for C&D(S) waste. Based on this it can be inferred that lower w/s ratio give higher degree of carbonation though some minimum amount of water is required for the reaction to occur in the first place. The extent of carbonation for different w/s ratios of C&D(S) waste sample, 0.3mm sieve size has been shown in fig 4. It can be seen that higher water content limits the carbonation. This can be attributed to the hindrance caused by water in the diffusion of CO₂ and as the gas-permeability of the sample is reduced, there is a decreased access to reaction

sites and so CO₂ cannot penetrate effectively to react to form carbonate.

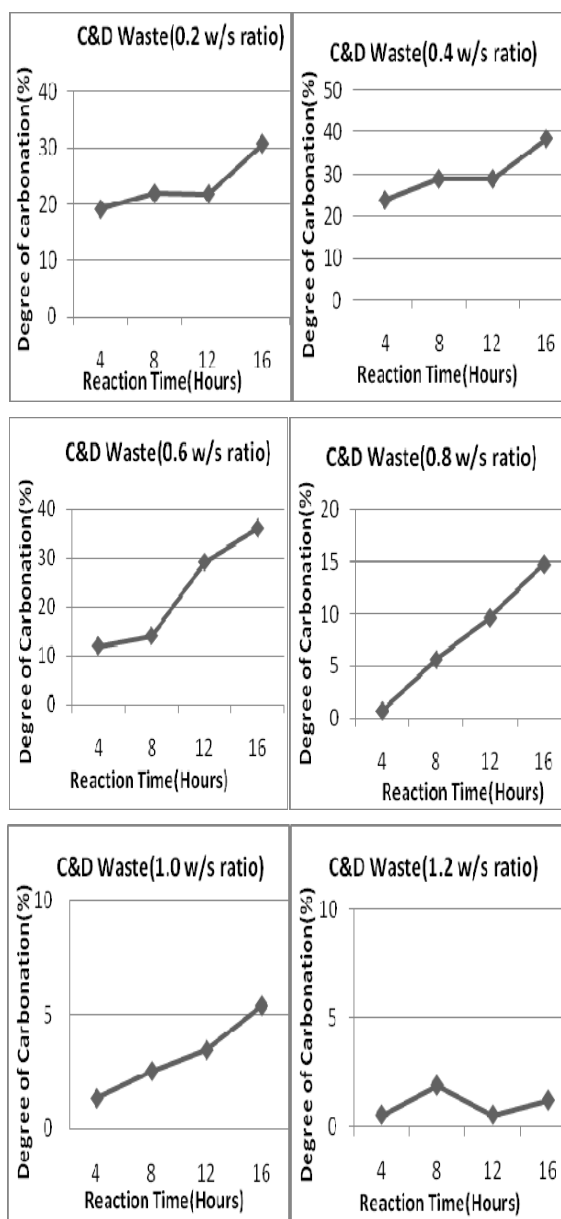


Fig. 3 Degree of Carbonation vs. Time for different w/s ratio (0.2 to 1.2) for C&D(S) waste sample(sieve size 0.3mm).

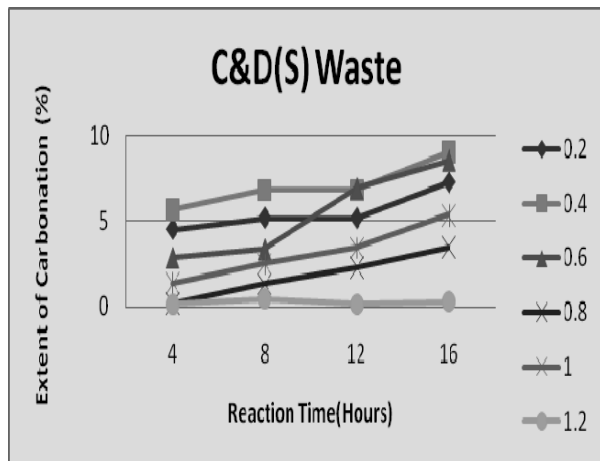


Fig. 4 Comparison of Extent of Carbonation of different w/s ratios for C&D(S) waste sample, 0.3mm sieve size.

The degree of carbonation of 38.44% for 0.4 w/s ratio emphasizes that only a percentage of the theoretical extent is actually realized when nothing is added to artificially induce the reaction. The theoretical extent takes into consideration the reaction of other oxides to form carbonates but the conditions of reaction are not ideal for the reaction of oxides such as MgO and other reactive oxides, which have the theoretical potential but require different physical treatments for the reaction. Even though other oxides react, they react in a comparatively lower quantity. The results of XRD shown in Fig 5, suggests that the primary product of carbonation reaction was calcium carbonate.

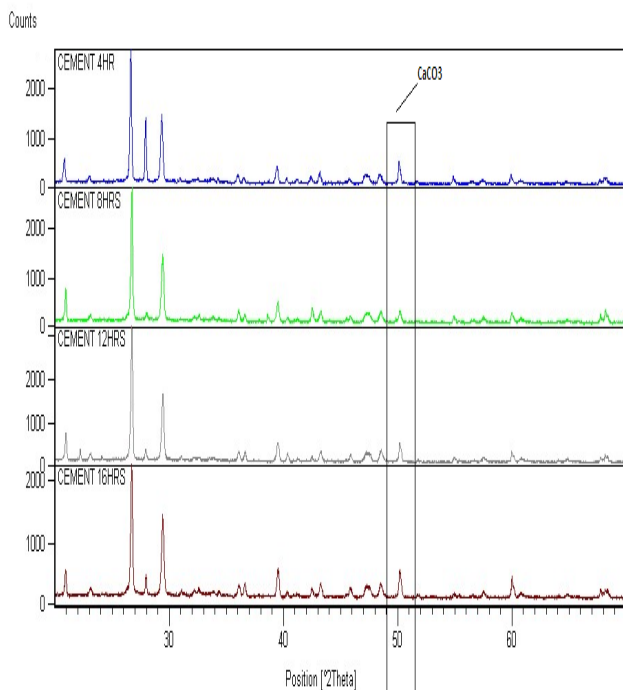


Fig. 5 X-Ray diffractograms of post carbonated C&D(S) sample

showing calcite formation during carbonation reaction, w/s ratio 0.4

C. Microscopic Analysis by SEM (Scanning Electron Microscopy)

The reaction products were analyzed morphologically by SEM analysis using an Evo 50 Zeiss instrument (at IIT Delhi), at 20kV and 10K. An EDS (Energy-dispersive X-ray spectroscopy) was also performed for the 16 hr post carbonated C&D(S) waste sample of w/s ratio 0.4, to confirm the carbonate precipitation. SEM analysis was carried out for both pre and post carbonated C&D(S) waste sample as shown in fig 6 below. The image in Fig 6(a) shows the microstructure of C&D(S) waste sample before its subject to carbonation reaction in batch reactor. Image given in Fig 6(b) shows the microstructure of post carbonated C&D(S) waste sample. The circled area in Fig 6(b) shows spiked growth, confirming carbonate precipitation as shown by researchers [23]. EDS carried on the 16hr C&D(S) post carbonated samples as shown in Fig 6(c), gives the increased Ca and C peak intensity, confirming the carbonate precipitation.

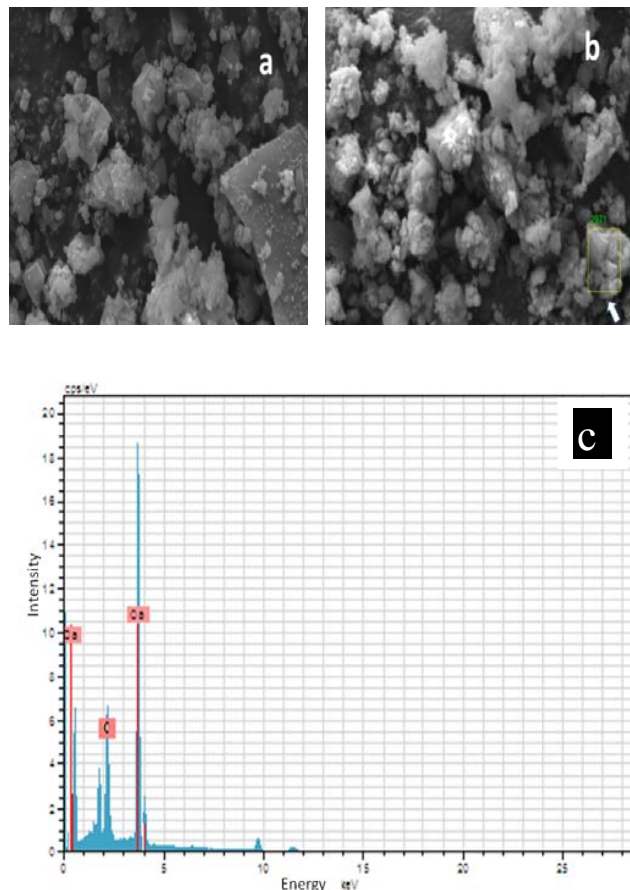


Fig. 6 (a) SEM image of pre carbonated C&D(S) waste sample. (b) Microstructure of post carbonated 16hr C&D(S) waste sample showing carbonate precipitation. (c) EDS spectra for 16hr sample showing high intensity Ca & C peaks.

D. Evaluation of extent of carbonation by Thermal Decomposition Analysis (TGA)

The TGA analysis of the post-carbonated C&D(S) waste was conducted for 0.4 w/s ratio. It was analyzed with respect to the TGA result of pre-carbonated sample. The carbonate content of the post-carbonated sample was found to be higher as compared to pre-carbonated sample. The difference in the percentages obtained from the above mentioned TGA results was expressed in the form of extent of carbonation. This extent of carbonation was found to be 9.462. The extent of carbonation obtained from direct mass gain in sample was observed to be 9.078. The comparable values validate the mass gain results.

IV. CONCLUSIONS

This paper demonstrates the evaluation of CO₂ sequestration potential of C&D waste. A series of batch experiments were conducted in a self fabricated batch reactor. Sample was exposed to constant CO₂ supply under standardized humidity, temperature conditions and varying w/s ratio. The results presented in the paper indicate that C&D waste could be an attractive and potential method to reduce the CO₂ emissions in the atmosphere. This experimentation investigation forms the first feasibility study to demonstrate that degree of carbonation achievable in C&D waste, for 16hr at w/s ratio of 0.4 is 38.44%. This confirms the possibility for utilization of C&D waste for future mitigation of CO₂. Thus it seems that the use of C&D waste holds promising for sequestration of CO₂ by carbonation reaction as it does not find economical importance in construction industry.

This approach is a breakthrough involving utilization of alkaline waste materials such as C&D waste, could help to reduce the cost for mineral CO₂ sequestration. The most important future application of such emerging technology will be utilization of such alkaline waste material as a final cover for the landfill. Final cover act as an important barrier for a municipal solid waste landfill. A large amount of landfill gas such as CH₄ and CO₂ is produced which contributes to the adverse environmental and climate changes. A certain amount of daily cover which is usually compressed soil layer is put everyday over the waste which prevents the waste from interacting with the air, thereby reducing the odor. The final landfill cover of alkaline waste material will reduce the landfill gas emission by their mineral sequestration. It will improve the environmental performance and cost-effectiveness of final landfill cover.

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