Carbon Dioxide Sequestration In Alkaline Waste

Anjali Gupta*, Arvind K. Nema**

*(Department of Civil Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016, India.
** (Department of Civil Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016)

ABSTRACT

The present study focuses on exploring an array of alkaline waste residues, procured from diverse sources as means for sequestering maximal CO_2. Alkaline waste residues undertaken for the study included: (1) Cement Bag Filter Dust, (2) Finished Cement Sample, (3) Marble Dust and (4) Baghouse Dust. Experiments were conducted in a self fabricated Carbonation reactor under 80% CO_2 concentration and at 40°C, water: solid (w/s) ratio of 0.2 to 1.2 with relative humidity in the reactor was maintained at 100%. Carbonation reactions were carried for 16hrs with sampling done every at intervals of 4hrs. The highest degree of carbonation achieved with Cement Bag Filter Dust was 25.84% at w/s ratio of 0.4 without any amendments to the waste material. Degree of carbonation achieved under similar conditions for other waste residue was 17.21% by Finished Cement Sample followed by Marble Dust 10.98% and finally by Baghouse Dust was 7.54%. It was concluded that a low w/s ratio of 0.4 was optimum for carbonation reaction due to increased access to reaction sites. Detailed experiments are further needed inorder to address the inconsistency in the observed carbonation achieved by different waste due to their heterogeneous nature.

Keywords - Carbon Sequestration, carbonation, Cement, mitigation, Waste Disposal

I. INTRODUCTION

Significant evidence on currently ongoing global warming and related climate modifications have been collected and reported by the scientific community in the last couple of decades, in particular by the U.N. International Panel on Climate Change [1]. An increase of almost 1 degree Celsius of the global average surface temperature of the planet since the mid 19th century, which was estimated to be the largest temperature increase occurred in the past 1300 years, has been confirmed [1], as well as other effects correlated to climate change such as the shrinking of mountain glaciers, the increase in the frequency and intensity of draughts and tropical storms and the rise of the average sea level.

The measured global warming has been associated to a sharp increase in the greenhouse gas effect, which is a natural phenomenon related to the presence of specific gases in the atmosphere, denominated greenhouse gases (mainly carbon dioxide, water vapour and methane) which absorb and reemit part of the infrared radiation emitted by the Earth's surface, trapping heat in the atmosphere. The significant enhancement of the greenhouse gas effect has been linked to the steep increase in CO_2 atmospheric concentrations registered since the beginning of the industrial revolution [1]. This increase has been primarily ascribed to human activities and in particular to the combustion of fossil fuels, which are estimated to produce about three quarters of anthropogenic CO_2 emissions [2]. The rest is mainly due to land use changes, especially deforestation. Several industrial processes like oil refining and the manufacturing of cement, lime, and steel are also significant sources of CO_2.

Carbon dioxide capture and storage (CCS) technologies have been indicated as one of the most viable and effective measures to reduce point-source emissions that could be applied in the short-medium term, at least until energy production will still rely on fossil fuels combustion [3]. This technology involves collection and concentration of the CO_2 generated by industrial or energy production plants, transport to a suitable storage site and subsequent storage in permanent, safe disposal sites such as geological formations, including saline aquifers, oil reservoirs and coal seams, or oceans [4, 5].

The purpose of CO_2 capture is to produce a concentrated stream of CO_2 at high pressure that can be transported to a storage site [3]. For the energy sector, there are three main approaches to capture the CO_2 generated from the combustion of fossil fuels, biomass, or mixtures of these fuels, depending on the process or type of power plant to which CO_2 capture is applied: post-combustion, pre-combustion, and oxy-fuel combustion systems. Post-combustion systems separate CO_2 from a flue gas stream, which generally contains 3-15% vol. CO_2, typically using a liquid solvent. This technique is currently used to absorb CO_2 from part of the flue gases generated from a number of existing power plants. It is also commercially used in the natural gas processing industry. Pre-combustion systems remove CO_2 before combustion by employing gasification, water-shifting, and CO_2 separation. This technology is widely applied for fertiliser manufacturing and hydrogen production. Oxy-fuel combustion systems use oxygen, instead of air, for

the combustion of the primary fuel to produce a flue gas that consists mainly of water vapour and CO_2. The extent of carbonation in alkaline wastes, such as coal fly ash, municipal solid waste incinerator ash, and steel slag has been investigated in preliminary experiments [6, 7, 8, 9] with favourable results. The utilization of alkaline waste materials provides several advantages: (1) waste materials supply a readily available source of calcium or magnesium mineral matter without the need for pre-processing; (2) they are typically fine-grained with high reactive surface areas; and (3) the environmental quality of the waste materials can be improved through pH-neutralization and mineral transformation [8, 10]. In addition, alkaline industrial wastes are typically generated at or near point sources of CO_2.

The present paper focuses on the study of feasibility of mineral carbonation in the selected alkaline wastes residues namely Cement Bag Filter Dust (CBF); Finished Cement Sample (FCS); Marble Dust (MD); and Baghouse Dust (BHD). The results were analyzed by determining their respective sequestration capacity based on their mineral and elemental complementary analysis. Carbonation reactions were carried out in a self fabricated Batch reactor. Samples were subjected to standardized conditions of temperature and humidity with sampling done at a regular interval of 4 hrs upto 16hrs. Further the optimum water: solid ration for different alkaline waste residue was determined by varying the water to solid ratio from 0.2 to 1.2. CO_2 sequestration capacity was established by comparing their respective degree of carbonation with respect to the reaction time. Difference in composition of the samples lead to the variability which further results in some uncertainty in the degrees of carbonation calculated for each of the sample.

II.   MATERIALS AND METHODS
2.1 SAMPLE COLLECTION
Alkaline waste samples of (CBF), (FCS), MD and BHD were procured from various sources. The samples were collected at the point of generation and placed in air tight bags for further analysis and experimentation.

2.2   CARBONATION REACTION USING BATCH REACTOR
The carbonation reaction was conducted in an acrylic carbonation reactor with the 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 reactor and shelves for keeping the samples. A CO_2 cylinder with a regulator was used to pass CO_2 into the carbonation reactor. A rotameter ensured the gas flow was set to 10 liters /minute. CO_2 was passed to stimulate a condition similar to infinite supply (ideal condition). The humidity was maintained to 100% using an aqueous chemical solution placed in troughs and placed inside the carbonation reactor.

The temperature in the reactor was maintained at 40°C for experimentation. The samples were oven dried at 100^0C to ensure there were no traces of initial moisture content. Thirty grams of CBF sample, forty grams of FCS sample, fifty gram of Marble Dust sample and fifty grams of BHD samples were used for carrying out the carbonation reaction. Distilled water was used to obtain the definite water to solids ratio (0.2 to 1.2). Thus the effect of different water to solids ratio at constant temperature, humidity and flow of CO_2 was determined.

The post-carbonated samples were oven dried at 100°C, crushed, mixed to a homogenous form, weighed and then stored at room temperature in air tight bags. The carbonation reaction results were noted at a regular interval of 4hrs, 8hrs, 12hrs and 16hrs for different water to solid ratio. The dry mass change of the samples was determined and was further used to calculate their respective degree of carbonation achievable with respect to reaction time.

2.3 MATERIAL CHARACTERIZATION
The theoretical extent of carbonation was calculated for the samples using the elemental compositions obtained from XRF analysis for their representative subsets. The estimation of theoretical extent of sequestration was based on stochiometric and the reactive oxide content in the waste. The theoretical stochiometric 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 similar to the estimate of Steinour [11] for concrete & mortars, as follows:

$$\%ThScCO_2 = 0.785(\%CaO - 0.56\%CaCO_3 - 0.7\%SO_3) + 1.091\%MgO + 0.71\%Na_2O + 0.468(\%K_2O - 0.632\%KCl) \qquad (1)$$

The stochiometric mass factors shown in above equation assume that all of the CaO will react with CO_2 to form $CaCO_3$, all the MgO will react to form $MgCO_3$ and all of Na_2O and K_2O will convert to Na_2CO_3 and K_2CO_3. Presence of initial $CaCO_3$, CaO in bounded form of $CaSO_4$, and K_2O in bounded form of KCl are discounted for. CaO was the main oxide in the waste samples (as illustrated by XRF results shown in TABLE 1 below), and the conditions of reaction were set for calcite production.

TABLE 1: ELEMENTAL COMPOSITION OF PRE-CARBONATED WASTE SAMPLES

Elemental Composition (%)	Alkaline Waste Residue			
	Cement Bag Filter Dust	Finished Cement Sample	Marble Dust	Baghouse Dust
SiO_2	21.74	22.63	5.57	5.94
Al_2O_3	6.52	8.81	0.46	2.23
TiO_2	0.46	0.1	0.07	0.15
Fe_2O_3	4.54	3.78	0.7	1.94
MnO	0.09	0.04	0.03	0.04
CaO	51.5	55.7	31.4	48
MgO	2.63	3.15	17.38	1.37
Na_2O	0.13	0.15	0.09	0.17
K_2O	0.54	0.45	0.19	0.38
P_2O_5	0.1	0.1	0.03	0.05
SO_3^{2-}	1.98	1.67	0.18	0.32
Cl^-	0.01	0.01	0.01	0.01
$CaCO_3$	28	19.1	27.44	25.4

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 equation 2 below.

$$W_g(t)=W(t)–W(t=0) \qquad (2)$$

Where W(t= 0) is the initial dry mass and W(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) as shown in equation 3 below.

$$\%CO_2(t)=[Wg(t)/W(t)]\times 100 \qquad (3)$$

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 ($ThCO_2$) based on initial composition of the sample as shown in equation 4.

$$E (t) =W_g(t) /[W(t=0)\times ThCO_2] \qquad (4)$$

III. RESULTS

In the following sub-sections, the degree of carbonation with respect to time for selected waste residue has been calculated and the potential candidate with highest CO_2 sequestered has been reported.

3.1 XRF ANALYSIS OF WASTE RESIDUES

The XRF analysis of pre-carbonated samples gave their elemental composition. The elemental composition of the pre-carbonated samples was analyzed with a Philips PW 2404 X-ray spectrometer (Cambridge, UK). Sample specimens were homogenized by grinding in a SPEX Shatterbox (Edison, NJ). Portions of the bulk sample were ignited at 980°C to a constant mass and then fused into glass disks with a LECO FX-503 automated fuser. The theoretical extent of carbonation was obtained by plugging in the percentage of various constituent compounds in the Equation 1. TABLE 2 below gives the stochiometric theoretical extent of carbonation achievable in selected alkaline residues. Inherent in this theoretical calculation is the assumption that the oxides in certain calcium and potassium phases are unlikely to react with CO_2 at selected temperatures and humidity. The calculated stochiometric theoretical extent in the BHD sample was found to be comparatively lower to that of CBF, MD and FCS can be attributed to its higher initial mass fraction of calcite.

TABLE 2: THE STOCHIOMETRIC THEORETICAL EXTENT OF CARBONATION ACHIEVABLE IN SELECTED ALKALINE RESIDUES

Alkaline Residue	Theoretical Stochiometric CO_2 Capture%
Cement Bag Filter Dust	30.24
Finished Cement Sample	38.16
Marble Dust	31.59
Baghouse Dust	28.13

3.2 CARBONATION OF ALKALINE WASTE RESIDUE

A simplified method was developed to estimate the sequestered quantity of CO_2 by carbonate precipitation. Once standardization was achieved, the carbonation of CBF, FCS, MD and BHD alkaline waste residue carried out in the batch reactor at 40°C maintaining a humidity of 100% with a flow of CO_2 at 10L/minute for 1 hour. The results are shown in Figure 1 for CBF, Figure 2 for FCS and Figure 3 for MD and Figure 4 for BHD.

The highest degree of carbonation achieved with Cement Bag Filter Dust in the CO_2 Reactor was 25.84% at w/s ratio of 0.4, 80% CO_2 and 16hrs duration without any amendments to the waste material. A lower water-to-solids ratio was obtained to have a higher degree of carbonation though some amount of water is required for the reaction to occur. Higher water content limits the carbonation. This can be attributed to the hindrance caused by water in the diffusion of CO_2 and as the gas-permeability of the sample is reduced, there is a decreased access to reaction sites and so CO_2 cannot penetrate effectively to react to form carbonate. The

stochiometric theoretical extent for the different samples types was determined as a function of water-to-solids ratio with respect to time. The optimum water: solid ratio for different samples was determined and their corresponding degree of carbonation was calculated.

CBF gave maximum degree of carbonation of 25.84% under given conditions of temperature, humidity and at 0.4 water: solid ratio as illustrated in Fig.1 below.
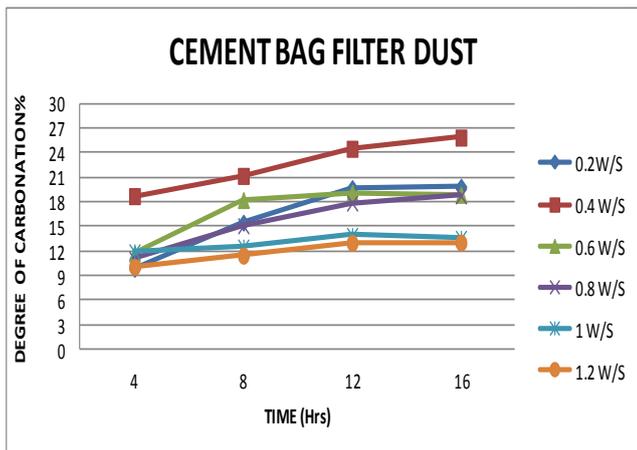

MARBLE DUST

Figure 3. Degree of carbonation in MD as a function of initial water-to solids ratio

CEMENT BAG FILTER DUST

Figure 1 Degree of carbonation in CBF as a function of initial water-to solids ratio

Degree of carbonation achieved under similar conditions with other waste residue investigated in the present study was 17.21% by FCS followed by MD 10.98% and finally by BHD was 7.54 % as illustrated in Fig. 2, Fig. 3 and Fig. 4 respectively. The degree of carbonation was observed to be greater at lower water: solid ratio of 0.4 due to increased access to reaction sites. Thus however higher water contents appear to decrease the overall sequestration extent by slowing or hindering the transport of CO_2 to reaction sites.
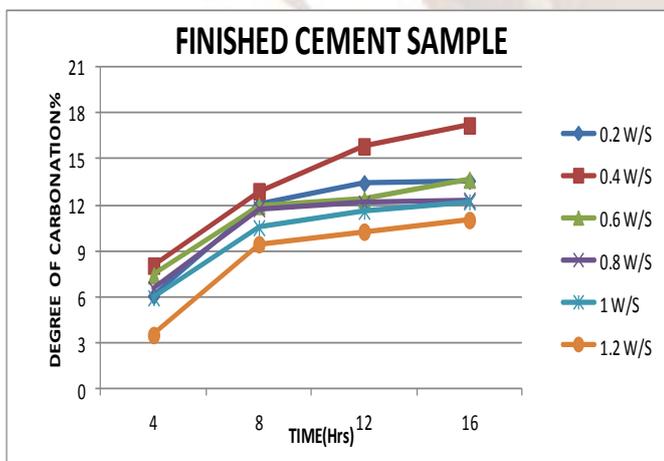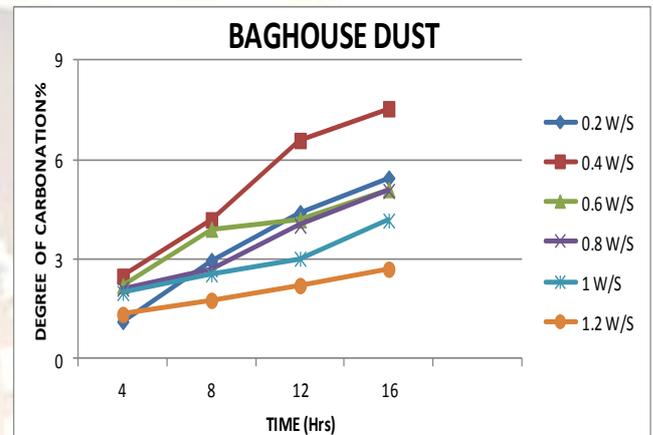

BAGHOUSE DUST

Figure 4 Degree of carbonation in BHD as a function of initial water-to solids ratio

IV. CONCLUSION

In conclusion, the results presented of this study reveal that the ex-situ mineral sequestration of CO_2 by carbonation of CBF, MD, FCS and MD could be an attractive method to reduce the CO_2 emission in the atmosphere. Comparative study of the degree of carbonation achievable in the selected waste with respect to time has been illustrated in Fig. 5 below.

FINISHED CEMENT SAMPLE

Figure 2 Degree of carbonation in FCS as a function of initial water-to solids ratio

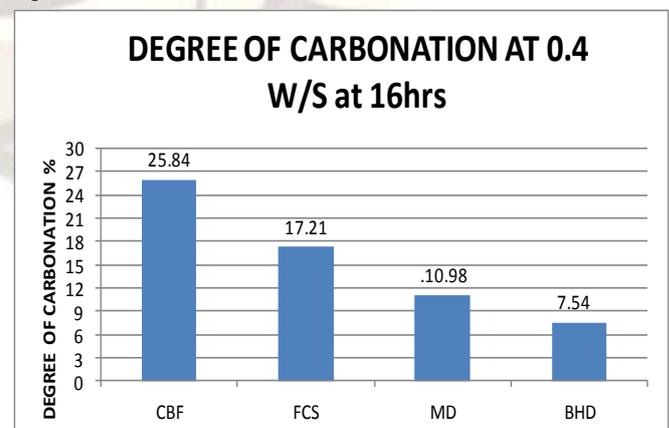

DEGREE OF CARBONATION AT 0.4 W/S at 16hrs

Figure 5 Comparison of degree of carbonation with respect to time e for selected waste sample at 0.4 water: solid ratio at the end of 16hrs.

It can be concluded that at w: s ratio of 0.4 and at end of 16hrs CBF shows the highest degree of carbonation when compared with other waste residues selected for the present study. The degree of carbonation was observed to be greater at lower water: solid ratio of 0.4 due to increased access to reaction sites.

This experimental investigation demonstrated that 1 ton of CBF, an industrial waste that contains about 51.1 wt. % of lime (CaO), could sequester up to 0.302 kg of CO_2 per kg of CBF with maximum degree of carbonation of 25.84% at the end of 16hrs at w: s ratio of 0.4. For FCS, an industrial product that contains about 55.7 wt. % of lime (CaO) could sequester up to 0.381 kg of CO_2 per kg of FCS with maximum degree of carbonation of 17.21% under similar conditions. For MD, an industrial waste that contains about 31.4 wt. % of lime (CaO) could sequester up to 0.315 kg of CO_2 per kg of MD with maximum degree of carbonation of 10.98%. Finally for BHD that contains about 48 wt. % of lime (CaO) could sequester up to 0.28 kg of CO_2 per kg of BHD with maximum degree of carbonation of 7.56 % under similar conditions.

This confirms the possibility to use these residues for CO_2 mitigation in punctual sources. Other advantages of the proposed method are (1) that the carbonation process takes place at low temperature (40°C) and reduces the energy costs of the process at industrial scale and, (2) the use of moderate pressure in the system does not require expensive materials for reactor design.

REFERENCES

[1]   IPCC (2007). Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. S. Solomon., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor, and H.L. Miller. (Ed.). Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

[2]   IPCC (2001). Climate Change 2001: The Scientific Basis. Contribution of Working Group I, Third Assessment Report of the Intergovernmental Panel on Climate Change (IPCC). J.T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, D. Xiaosu, (Ed.) Cambridge University Press, UK.

[3]   IPCC (2005). IPCC special report on carbon dioxide capture and storage. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

[4]   K.S. Lackner. Carbonate chemistry for sequestering fossil carbon. *Annual Review for Energy and the Environment*, *27*, 2002, 193-232.

[5]   K.S. Lackner. Climate change: a guide to CO_2 sequestration. *Science*, *300*, 2003, 1677-1678.

[6]   D.J. Fauth, Y. Soong, and C.M. White. Carbon Sequestration Utilizing Industrial Solid Residues. Symposium-American Chemical Society, *Division Fuel Chemistry*, 2002, 37- 38.

[7]   M.F. Bertos, X. Li, S.J.R. Simons, C.D. Hills, and P.J. Carey. Investigation of Acceleration Carbonation for the Stabilisation of MSW Incinerator Ashes and the Sequestration of CO_2. *Green Chemistry, 6*, 2004a, 428-436.

[8]   M.F. Bertos, X. Li, S.J.R. Simons, C.D. Hills, and P.J. Carey. A Review of Accelerated Carbonation Technology in the Treatment of Cement-Based Materials and Sequestration of CO_2. *Journal of Hazardous Material , B112*, 2004b, 193-205.

[9]   W.J.J. Huijgen, G.J. Witkamp, and R.N.J. Comans. Mineral CO_2 Sequestration by Steel Slag Carbonation. *Environmental Science* and. *Technology*, *39 (42),* 2005, 9676-9682.

[10] W.J.J. Huijgen and R.N.J. Comans. Carbon Dioxide Sequestration by Mineral Carbonation Literature Review. *Energy Resource Center of the Netherlands,* 2003, ECNC- 03-016, 2003. Available at www.ecn.nl (Accessed 29 December 2010).

[11] H.H. Steinour. Some Effects of Carbon Dioxide on Motars and Concrete – Discussion, Concrete Briefs, *Journal. American Concrete Institute,* 1959, 905-907.