

Direct Mineral Carbonation of Coal Fly Ash at Varying Low Pressure Conditions

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ABSTRACT

Climate change and its associated impacts have stirred global attention towards the rising carbon dioxide emissions. In this regard, carbon capture and storage technology is viewed as a promising option towards climate change mitigation. Among the various approaches available in this technology, direct mineral carbonation of industrial alkaline solid residue is an attractive tool for large scale industrial applications. In this work, coal fly ash one of the major solid wastes produced from the power sector of the country was considered for carbon capture. Direct mineral (dry and wet) carbonation of coal fly ash has been studied at room temperature and at varying initial CO₂ partial pressure conditions (1-10 bar). The carbonation experiments were conducted in a batch reactor with 99.99% pure CO₂ gas for a time period of 1 h. On completion of the experiment, the net carbon increase of the waste was analyzed using total organic carbon analyzer. The maximum net carbon increase that was realized at the initial CO₂ partial pressure of 10 bar (maximum value used) is 7.18 g/ kg through dry carbonation. In case of wet carbonation the maximum achieved is 11.18 g/kg at 6 bar. Of the two routes considered, better results (55.3%) were obtained for the later one in terms of carbonation efficiency which emphasis the significance of water in the reaction process. The results suggest that for the specified reaction time the carbonation process in both the routes (wet and dry) is pressure dependent.

Keywords- Carbon dioxide; Climate change; Mineral carbonation; Coal fly ash

1. INTRODUCTION

The emission of greenhouse gases (GHGs) particularly CO₂ into the atmosphere is the reason behind global warming which subsequently induces changes in global climate. Even if the emission of the CO₂ gas is stopped at current levels, the impacts of climate change are likely to persist for years to come. Thus reduction of CO₂ emissions and thereby climate change mitigation is of utmost global importance [1]. In this context, carbon capture and storage (CCS) technology is viewed as a potential tool with many promising routes to tackle climate change and lead the energy sector towards sustainability [2]. India being an emerging economic power, its energy demand is projected

to increase drastically [3]. The country is in need of technologies such as CCS in order to cope up with climate change and minimize its CO₂ emissions [4].

Mineral carbonation is a promising approach unlike other storage options under the CCS technology owing to the fact that the CO₂ stored will not be released to the atmosphere [5]. In direct mineral carbonation, the alkaline metal oxides present in the minerals are made to react with CO₂ in dry or wet route [6]. Yet the major drawback in this technology is the consequences associated with the mining of the minerals and the disposal of the end products formed in the process [5]. Thus the need for an alternative material to capture CO₂ emerged out and industrial alkaline solid residues came into the limelight as an attractive resource whose disposal is difficult otherwise. These residues are alkaline, easily accessible and also available in abundant quantities near the point source of the CO₂ emissions. Alkaline wastes such as steelmaking slags, cement klin dust, red mud, coal fly ash (CFA), paper mill waste etc has been subjected to direct mineral carbonation and the majority of these studies are in laboratory scale concerning process optimization [6]. In addition to the fact that the process promises permanent storage of CO₂, it also renders the alkaline waste eco-friendly [7].

CFA is one of the major industrial wastes generated in the country whose per annum production is 112 million tons and is supposed to increase in future. Of the total CFA produced, only 38% is being utilized in the construction sector whereas the remaining is land filled [8]. It is the by-product obtained from power plants which are the major point source emitters of CO₂ in the country. Though its major composition is silica and aluminium, it also consists of calcium and magnesium oxides that could be used for storing carbon [9]. Attempts have been made to optimize the different process parameters in aqueous carbonation of CFA with water [10, 11] and in brine solution [12] in order to realize the most efficient system and its parameters. A pilot scale testing using CFA with direct flue gas through accelerated mineral carbonation has also been demonstrated in a power plant after successful lab scale study [13]. Thus there exists a scope to study mineral carbonation of CFA which is generated in abundant quantities in the country and optimize the process parameters. The current study is to perform direct mineral carbonation of CFA at room temperature with 99.99% CO₂ gas. The objective of the work was to evaluate the carbonation potential of CFA and to determine the effect of initial CO₂ partial pressure on carbonation process.

2. MATERIALS AND METHODS

2.1 Materials

CFA was collected from a power plant situated in Tamilnadu, India. The waste thus obtained was dried to constant weight and then stored in air tight containers. The CO₂ gas used in the study was

100% pure gas purchased from Indogas, Chennai. X-ray fluorescence (XRF) analysis was performed in Bruker-S4 Pioneer WD-XRF instrument to determine the composition of CFA.

2.2 Carbonation experiments

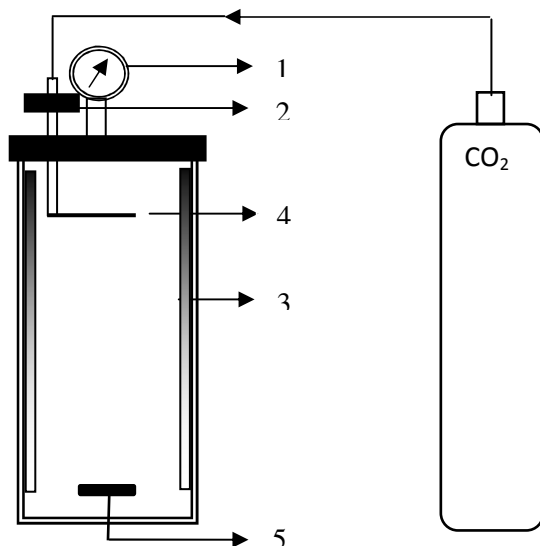


Fig. 1 Schematic diagram of the experimental set up used for carbonation studies
1- pressure gauge; 2- gas inlet valve; 3- baffle; 4- gas inlet port; and 5- magnetic pellet

Experiments were conducted in a batch reactor made up of stainless steel with the maximum operating volume of 1 L as shown in figure 1. The reactor consists of four baffles to provide mixing and a pressure gauge to monitor pressure inside the reactor. Known quantity of the CFA was taken in the reactor and then filled with the CO₂ gas from the cylinder fitted with the regulator. Each run was carried out at specific initial CO₂ partial pressure at room temperature for a time period of 1 h. In the case of wet capture studies, the CFA water slurry (L/S ratio-15) was stirred at 500 rpm using magnetic pellet and placing the reactor on magnetic stirrer. On completion of each run, the slurry was filtered and the solid product was separated, oven dried and then analyzed. In the case of dry carbonation, the solid product was directly taken for analysis. All the experiments were conducted in triplicates and after each run the carbonated product was analyzed for carbon.

2.3 Material Characterization

About five representative samples were analyzed for carbon content taken from the solid product obtained from each run of the experiment. The carbon content was determined using Analytikjena make multi N/C® 2100 S BUTOC Analyzer and solid module HT 1300, Germany.

3. RESULTS AND DISCUSSION

3.1 Carbonation of CFA

Carbonation of CFA in dry and wet conditions was performed for the fixed reaction time of 1 h at room temperature. After the completion of the experiment, the pressure reading inside the reactor dropped which may be due to the carbonation process. The carbonation process is dependent on the partial pressure as indicated in Figure 1 at a specified temperature in accord to Henry's law (Eq. 1).

$$P \propto C \quad (1)$$

The amount of CO₂ gas molecules in collision with the waste/waste slurry is directly proportional to the partial pressure of the gas above it. This may be the reason behind the observed better results at high initial CO₂ partial pressure values [11]. Here P is the partial pressure of the gas above the solution and C is the concentration of the dissolved gas. Figure 2 shows the comparison in net carbon increase observed through both routes in the carbonated samples at varying initial CO₂ partial pressure. As seen in the figure, the net carbon increase was maximized in wet route than in the dry route for the specified reaction time. In the case of dry carbonation route the net carbon increase in CFA was found to be increasing with increasing pressure value and reaching its maximum value of 7.18 + 0.27 g/kg at 10 bar. In wet carbonation approach, the carbon content in the CFA increased up to certain level of pressure after which it gets saturated as indicated by the curve. The maximum value of net carbon increase reached was 11.18 + 0.37 g/kg at 6 bar.

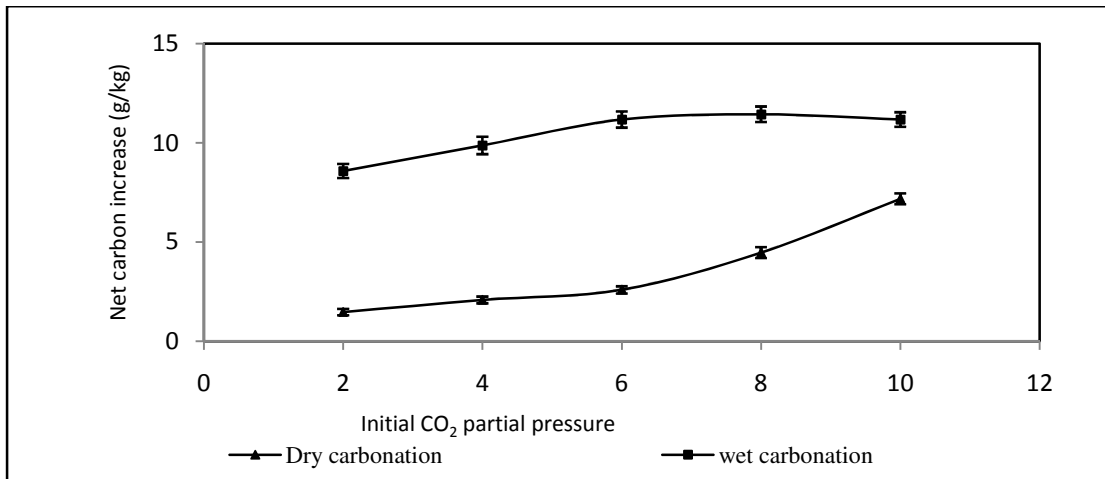


Figure 2: Net carbon increase in CFA at varying initial CO₂ partial pressure (Reaction time - 1 h, Room temperature and L/S ratio-15 for wet carbonation)

In dry carbonation, the alkaline oxides directly react with CO₂ gas to form carbonates under the controlled atmosphere as shown in Eq. 2 and 3 which is the mechanism by which the process takes place [6].



With regard to wet carbonation, CO₂ dissolution takes place due to the presence of water in the system as indicated in Eq. 4 [6]. This may be the reason behind the enhanced level of carbonation achieved in this route.



These results suggest a simple mechanism for aqueous carbonation involving hydration of CaO and its conversion into carbonates (Eq. 5 and 6) [10].



3.2 Carbonation Efficiency

The theoretical sequestration capacity was found using the chemical composition of CFA and applying Stenoir's formula (Eq. 7) [12].

$$\text{CO}_2 (\%) = 0.785 (\% \text{ CaO} - 0.7\% \text{ SO}_3) + 1.09\% \text{ MgO} + 0.71\% \text{ Na}_2\text{O} + 0.468\% \text{ K}_2\text{O} \quad (7)$$

$$\text{Carbonation Efficiency} = (\text{Actual} / \text{Theoretical}) \times 100 \quad (8)$$

XRF analysis revealed that the CFA particles consists of 6.74% of CaO, 2.22% of MgO, 3.29 % of SO₃, 1.38% of Na₂O and 1.13% of K₂O. Assuming that all the alkaline oxides that are available in CFA will undergo complete carbonation, the theoretical sequestration capacity of CFA comes to the value of 74.11 g of CO₂/ kg i.e 1 kg of CFA could sequester 74.11 g of CO₂. For calculations, actual sequestration capacity of CFA at their maximum values i.e 26.33 g of CO₂/kg (at 10 bar) for dry route and 41.0 g of CO₂/kg (at 6 bar) for wet route was taken. These values were obtained from the net carbon increase achieved in that particular run. The carbonation efficiency achieved in CFA was calculated using Eq. 8.

The carbonation efficiency achieved in both the routes is presented in Figure 3. About 55.32% of efficiency was achieved through slurry phase aqueous carbonation and 35.52% in gas-solid carbonation. These results confirm that direct mineral carbonation of CFA at low pressure conditions (1-10 bar) and at room temperature is a realizable process with significant carbonation efficiency. This is in agreement with the pilot scale study reported with CFA, in which it was subjected to gas-solid carbonation at 1.151 bar with real flue gas wherein carbonation was achieved at room temperature and low pressure conditions [13].

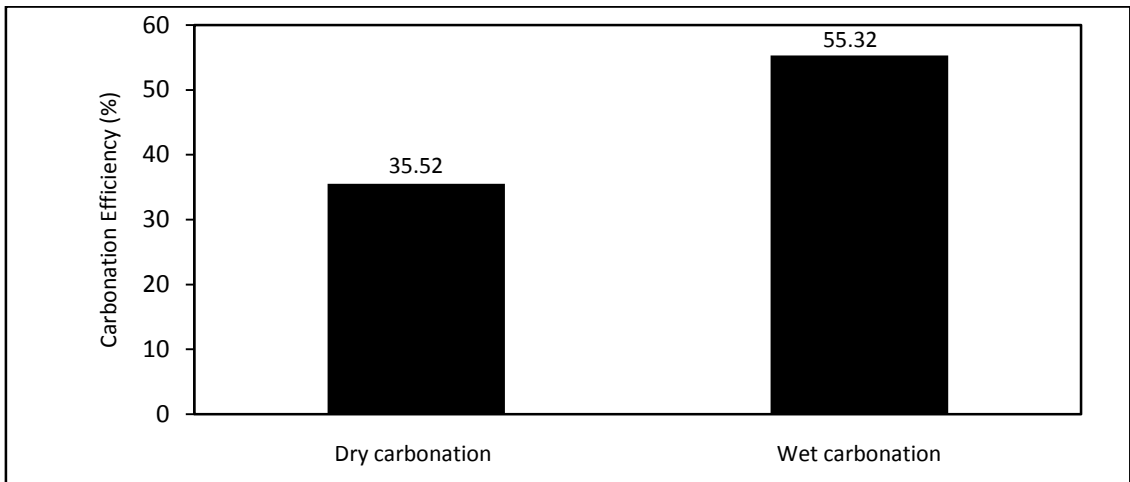


Figure 3: Maximum carbonation efficiency achieved in both the carbonation routes

4. CONCLUSION

This study provided an insight into the direct mineral carbonation of CFA at varying pressure conditions and at room temperature. The carbonation process was observed to be dependent on initial CO_2 partial pressure for a fixed reaction time whether it is wet or dry route. The optimum initial CO_2 partial pressure for both the routes has been determined at room temperature and for the reaction time of 1 h. The maximum carbonation efficiency of CFA achieved is 55.3% with the sequestration capacity of 41 g of CO_2/kg . When applied to the net annual production of CFA (112 million tons) in the country, the amount of CO_2 that could be sequestered is 61.94 million tons/annum.

5. ACKNOWLEDGEMENT

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