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ORIGINAL PAPER

# Carbon capture and storage using coal fly ash with flue gas

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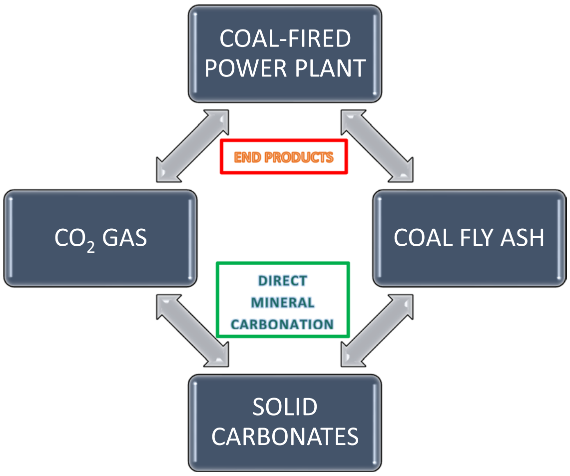
## Abstract

Rising $CO_2$ emissions call for actions to urgently address climate change and its impacts. To avoid the harmful consequences of climate change, limiting anthropogenic emissions of $CO_2$ are a sensible response recognized by the global scientific community. Carbon capture and storage technologies are an integral part of the climate change mitigation portfolio. Among the various technologies, mineral carbonation shows promising potential as it is safer and offers a permanent solution for carbon capture and storage in the form of solid carbonates. In this regard, direct mineral carbonation of alkaline solid residues is viewed with global interest as they offer permanent and leakage-free storage of $CO_2$. In this research work, $CO_2$ sequestration using Indian coal fly ash (class F type- $CaO < 10\%$) has been studied through the direct mineral carbonation process using flue gas concentration of $CO_2$. Response surface methodology was used to design the carbonation experiments through gas–solid and aqueous routes. Aqueous carbonation of coal fly ash at optimum conditions (temperature-61.6 °C, pressure-48.7 bar, liquid/solid ratio-13.35, reaction time-50 min) resulted in a reduction of about 23% in the concentration of $CO_2$. The waste exhibited a maximum sequestration capacity of 50.72 g of $CO_2$/kg under aqueous carbonation and 20.03 g of $CO_2$/kg under gas–solid carbonation. Both temperature and pressure were found to be significant factors impacting the gas–solid carbonation process. In aqueous carbonation, temperature and liquid/solid ratio were the significant factors. The carbonation process was evidenced using Fourier-transform-infrared spectroscopy, X-ray diffraction, and scanning electron microscope studies. The results suggest that Indian coal fly ash could be considered a potential feedstock for sequestration of $CO_2$ with flue gas and requires further improvement for large-scale implementations.

## Graphic abstract



**Keywords** Carbon capture and storage technology · Carbon dioxide · Climate change · Mineral carbonation · Coal fly ash · Flue gas

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## Introduction

Fossil fuel-based energy sector and industrial processes together contribute the largest share (78%) of global greenhouse gas emissions (IPCC 2014). The world witnessed a rise in global energy-related $CO_2$ emissions by about 1.7% in 2018 and it is expected to increase further in the coming years (IEA 2019). India emits 3202 $tCO_2e$ per year, with the energy sector holding the biggest stake (68.7%) (USAID 2018).

For effective reduction in $CO_2$ emissions, implementation of carbon capture and storage (CCS) technologies is now essential, and therefore key to possible mitigation of climate change (Veetil and Hitch 2020). Mineral carbonation technology, an emerging option for CCS, provides an environmentally benign and permanent solution for $CO_2$ (Pan et al. 2012). Here, the slow natural weathering process of minerals and wastes that contain alkaline metals are accelerated to form solid carbonates in a controlled atmosphere (Lackner et al. 1995). Ex-situ mineral carbonation is even more promising as it can be directly retrofitted to the existing point sources of $CO_2$ emissions (Veetil and Hitch 2020) and also in places where geological storage is not feasible (Saran et al. 2018). This technology does not require post-monitoring, separation, and transport of $CO_2$ from the emission sources and all the associated costs involved which is the major issue with in-situ mineral carbonation (Bobicki et al. 2012).

In ex-situ CCS technology, mitigation of $CO_2$ emissions is attainable through both direct and indirect mineral carbonation. Of the two, the direct method is an emerging post-combustion CCS technology in which carbon is stored permanently without using much energy and chemicals unlike the indirect method (Bobicki et al. 2012). Direct mineral carbonation involves the reaction of alkaline metal oxides with $CO_2$ gas, either in the gas-solid route or aqueous route (Saran et al. 2018). Regarding the feedstock selection for carbonation, the use of minerals is less recommended as the laboratory and pilot-scale studies have highlighted extensive energy and cost requirements, thus making it unpopular for the industrial scale of implementation (Veetil and Hitch 2020).

Further, utilization of alkaline solid residue (ASR) for the carbonation process has been established to provide more benefits than minerals as these wastes are mostly available at the proximity of point sources of $CO_2$ emitters and are available at free of cost (Pan et al. 2012). The various industrial ASR identified to sequester $CO_2$ gas by the global scientific community includes coal fly ash (CFA) (Montes-Hernandez et al. 2009), combustion residues (Rao et al. 2007), steelmaking slag (Chiang and Pan 2017), red mud (Dilmore et al. 2008), lime mud (Perez-Lopez et al. 2008), cement kiln dust (Huntzinger et al. 2009) and oil shale wastes (Uibu et al. 2011). Most of these studies report the sequestration potential of ASR at laboratory-scale and the influence of various process parameters on carbonation. Meanwhile, a carbon capture plant utilizing red mud has been successfully built and maintained by a refinery in Australia (Alcoa 2012) which showcases the feasibility of developing this method at a large-scale. A successful demonstration study has also been attempted in the US with CFA (Reynolds et al. 2014). Recently, there have been promising results in testing the use of steelmaking slag at a pilot-scale level in Taiwan (Chiang and Pan 2017) and Finland (Said et al. 2016).

CFA is an ASR generated from thermal power plants. Combustion of coal produces CFA as a by-product which is collected from the exhaust gases using air pollution control equipment. CFA, a major industrial ASR generated in India (Pappu et al. 2007), contains major oxides of Si, Al, Fe and Ca (Montes-Hernandez et al. 2009). The annual production of CFA was about 217 t for the year 2018–19. The annual utilization rate remained at 60% for many years and only recently, a utilization rate of about 78% was achieved for the year 2018–19. Despite various efforts taken by the energy sector to achieve 100% utilization of CFA over the past decade, the goal has remained a distant dream as large quantities of the waste generated continue to be ultimately dumped in landfills (Central electricity Authority 2020).

Worldwide, there have been attempts to study direct mineral carbonation of CFA with pure $CO_2$ gas. The concept of utilizing CFA as an additive to brine solutions aimed at sequestration of $CO_2$ was first attempted by Soong et al. (2006). Later, CFA was used as it is for CCS in water by Montes-Hernandez et al. (2009). Aqueous carbonation of CFA water slurry with pure (100%) $CO_2$ gas was also reported by few researchers. Ukwattage et al. (2013) reported testing of Victorian CFA and optimization of two operational parameters, namely, initial $CO_2$ pressure and liquid/solid (L/S) ratio. Ukwattage et al. (2015) further studied the effect of temperature on the carbonation of three different fly ashes. Jaschik et al. (2016) also determined the sequestration potential of CFA and two other ashes from a Polish plant and reported the effect of L/S ratio, temperature and pressure on the aqueous carbonation process. Chinese CFA was tested for its carbonation performance and the underlying mechanism by Ji et al. (2017). They also studied the influence of the L/S ratio, temperature, and gas flow rate on the aqueous carbonation of CFA. Further, they extended their work by studying fly ashes from five different plants to understand the carbonation process and its effect on CFA (Ji et al. 2019). Their study suggests that fly ashes with high content of Ca and Mg bearing phases exhibited superior carbonation performance. Also, the kinetics of the carbonation process are highly dependent on the mineral phases contained in CFA with calcium bearing reactive phases showing high reactivity with $CO_2$ gas.

Muriithi et al. (2009) examined the carbonation potential of South African CFA in brine. They optimized the process parameters, namely, L/S ratio, particle size, temperature, and pressure using statistical methods. They also confirmed the superior efficacy of using brine solutions over water as a medium for carbonation since the former also contributes toward the total available calcium in the CFA slurry (Nyambura et al. 2011). The same research group also attempted an interesting study by comparing ex-situ aqueous carbonation of the CFA with in-situ natural weathering process occurring in a wet ash dam (Muriithi et al. 2013). The study results revealed that the slow natural process of weathering in ash dams could also contribute a significant share in overall carbon capture and storage by a power plant.

Recently, the gas-solid carbonation of CFA is also gaining considerable attention from researchers. Cwik et al. (2018) studied dry and moist carbonation of CFA collected from a power plant situated in Greece. They estimated that 21% of its $CO_2$ emissions from the plant could be reduced using this technology if scaled up. The study also determined the effect of temperature and pressure on the carbonation of CFA. Altiner (2018) studied five different Turkish fly ashes from different power plants and determined their sequestration potential at ambient temperature with varying pressure and reaction time. Liu et al. (2018) reported gas-solid carbonation of CFA with steam addition and at various concentrations of $CO_2$ gas (5–100%). An interesting study by Kim and Kwon (2019) reported a semi-dry method of direct mineral carbonation using CFA and its possible advantages over the aqueous carbonation method.

Carbonation of CFA with real flue gas has been studied by Reddy et al. (2011). They performed mineral carbonation of CFA in a fluidized bed reactor with the flue gas ($CO_2$:12%–14%) in a power plant located in the USA. Preliminary studies were followed by pilot-scale studies, wherein, test runs were conducted to optimize the process parameters. They achieved about 30% reduction in the concentration of $CO_2$ (Reddy et al. 2010). Based on the results obtained, they further conducted a successful demonstration-scale field testing in the same plant (Reynolds et al. 2014).

In summary, most of the research studies aimed at optimization of the carbonation process involving CFA following a waste-specific approach. The extent and efficiency of the carbonation process are highly dependent on the composition of CFA. There are still knowledge gaps in understanding the carbonation process of CFA and methods for maximizing its sequestration potential also remain understudied.

Moreover, efforts to convert carbonated CFA into a valuable product such as a compost amendment (Ukwattage et al. 2016) have been examined to realize a cost-benefit. Recently, CFA is also utilized for an integrated process of carbon capture and green synthesis of a usable product. The products that are so far reported include aggregates (Ramme et al. 2010), mesoporous $Al_2O_3$ (Yan et al. 2018), nanoparticles (Cheng et al. 2020) and zeolite (Monasterio-Guillot et al. 2020).

Meanwhile, global energy demand is estimated to increase by more than a quarter by the year 2040, even if the energy sector strictly follows a sustainable path informed by sound policies (IEA 2019). India leads the growth profile in energy demand alongside other developing nations, which mandates the need for technologies that mitigate the issues created by the growing energy demand (IEA 2019). While research and development of CCS technologies are at a preliminary stage in the country, no research data are available yet on the evaluation of the use of Indian CFA for the direct mineral carbonation process with real flue gas. Recently, an isolated laboratory study was reported by Tiwari et al. (2020) demonstrating the carbonation potential of a mixture containing cement and CFA. Previously, we examined the sequestration potential of CFA by direct mineral (both gas-solid as well as aqueous) carbonation in laboratory-scale using pure (100%) $CO_2$ gas under mild process conditions of pressure (1–10 bar) at room temperature. Optimization of process parameters, namely, initial $CO_2$ pressure, reaction time and liquid/solid (L/S) ratio of the slurry was attempted by employing the classical method of varying one parameter at one time (Dananjayan et al. 2016).

Statistical methods have been gaining the attention of the scientific community for a while now, wherein the effect of each factor on other factors and their interactions could be determined and thereby saving time and cost (Bezerra et al. 2008). Response surface methodology (RSM) is one such tool used extensively to design scientific research studies and to optimize various process parameters (Irfan et al. 2020). Recently, the practice of RSM in designing the mineral carbonation process of ASR has been attempted. Grace et al. (2012) performed statistical testing of direct aqueous carbonation of CFA in brine with pure $CO_2$ gas. They employed a d-optimal factorial design of RSM and used factors such as temperature, L/S ratio, particle size, and pressure. Irfan et al. (2020) attempted to study the aqueous mineral carbonation of cement kiln dust using RSM.

Thus, to sum up, except for a few studies carried out with real flue gas, most of the studies have focused on the direct mineral carbonation of CFA with pure $CO_2$ gas. In the development of CCS technology, the use of real flue gas or $CO_2$ gas in flue gas concentration is the way forward. Also, the carbonation potential of Indian CFA which, majorly falls in Class F type (CaO < 10%), has neither been explored nor reported especially, with real flue gas. Moreover, statistical testing of the process parameters can further help to understand the carbonation process. This study, therefore, focuses on the direct mineral carbonation of Indian CFA with flue gas concentration of $CO_2$ at high process conditions (pressure > 10 bar) using RSM. The effect of individual parameters and their interaction on the process will be studied. The objective is to investigate the sequestration potential of Indian CFA by gas-solid and aqueous carbonation with flue gas concentration of $CO_2$.

## Materials and methods

### Overall procedure

Figure 1 presents the overall procedure of the research work as a flow chart. CFA was collected from its generation site and characterized initially to study the composition of the waste. 'Materials' section deals with the various analyses performed on CFA in its solid particle form and as a slurry. The next step is the design of experiments for conducting carbonation (both gas-solid and aqueous) studies using RSM. Gas-solid carbonation (two parameters) and aqueous carbonation (three parameters) experimental runs were generated from the software and further explained in the 'design of experiments' section. After designing, the carbonation experiments were carried out in the reactors as described in the 'experimental setup' section. This section is followed by the 'carbonation experiments' that elaborate on the procedure followed to conduct the batch experiments. After every experiment, the concentration of $CO_2$ was analyzed to calculate "reduction (%)" and covered in the 'gas analysis' section. The response (reduction (%)) obtained from these experiments was fed into the RSM design to obtain the global optimum solution and to determine the importance of each parameter and the interaction between them. Further, the effect of reaction time was determined as depicted in the flowchart under the optimum conditions thus obtained from the software. Finally, characterization studies of the carbonated CFA are reported in the sections 'carbon analysis of CFA' and 'post characterization of CFA'.

### Materials

CFA (2 years old) was collected from the dumpsite of a power plant in Tamilnadu, India. The ASR was gray in color and of fine texture, as shown in Fig. 2 with a grain size of < 700 µm. The initial moisture content of the CFA particles was 28%. Particles had an average Brunauer–Emmett–Teller surface area of 14.47 $m^2/g$ determined using Quantasorb surface area and a pore size analyzer. X-ray fluorescence (XRF) analysis to determine the composition of CFA particles was performed using the Bruker-S4 Pioneer WD-XRF instrument. It showed that CFA consisted mainly of silicon (41.83%), aluminum (18.39%), iron (9.16%) and calcium (6.74%) oxides. Oxides of sulfur (3.29%), magnesium (2.22%), sodium (1.38%), potassium (1.13%), titanium (1.03%) and phosphorous (0.41%) were present in low quantities. Traces (0.38%) of Mn, Sr, Ba, Cl, V, Zr, Cr, Ni, Zn and Cu were also present in the ASR. Loss of ignition was determined to be 13.96%. The alkaline nature of ASR was thus confirmed by the presence of a high quantity of metal oxides such as calcium and magnesium, constituting about 9% of the total composition of CFA. Mineralogy of CFA was determined using a PANalytical X'pert powder X-ray

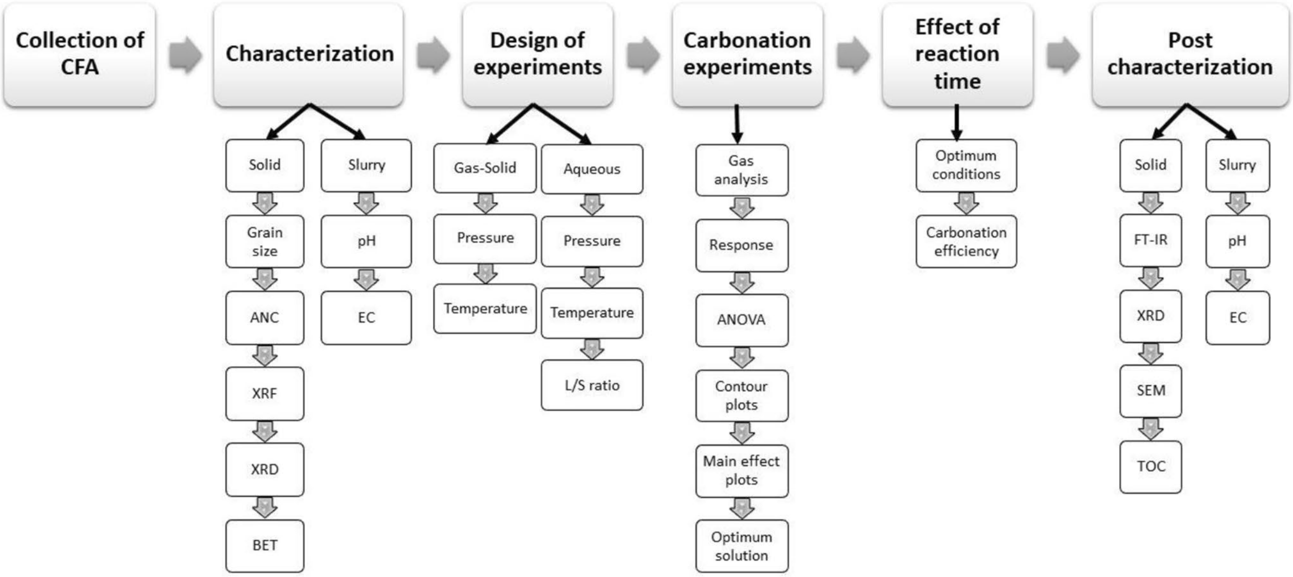


**Fig. 1** Overall procedure of the research work

**Fig. 2** Picture of CFA used for the study

diffraction (XRD) system. The major mineral phases identified were mullite ($Al_2O_3SiO_2$), magnetite ($Fe_3O_4$), hematite ($Fe_2O_3$) and quartz ($SiO_2$). As evidenced in the XRF analysis, the major mineral phases identified in CFA are mullite and quartz belong to the elements aluminum and silica, followed by iron. Minor phases such as lime (CaO), calcite ($CaCO_3$) and portlandite ($Ca(OH)_2$) were also detected. The complete characterization results of the ASR are already published in our previous research work (Dananjayan et al. 2016). These results suggested that CFA is made of small-sized finely divided particles that are highly alkaline suitable for $CO_2$ sequestration.

CFA mixed with water in the L/S ratio of 1:10 was subjected to characterization studies such as acid-neutralizing capacity (ANC), pH, and electrical conductivity (EC). ANC of CFA slurry was determined to be 0.07 meq/g indicating the alkaline nature of the waste. pH was found to be 9.41, and EC was about 2.84 mS/cm.

## Design of experiments

Before conducting the experiments, the Central composite design (CCD) of the statistical tool was used to design the experiments. Minitab version 16 software was used for the purpose. The interaction of two parameters (pressure and temperature) on gas-solid carbonation was studied using the CCD. In the case of aqueous carbonation, the significance of three (pressure, temperature and L/S ratio) operational parameters were determined. CCD employs Eq. (1) to determine the total number of experimental combinations (*N*), in which *k* is the number of factors, and $c_p$ is the number of replications at the central point (Bezerra et al. 2008). A full factorial design of 14 experimental runs was performed for the gas-solid carbonation study, while it is 20 runs for aqueous carbonation. In the model, the independent variables were coded according to Eq. (2), in which $x_i$ is the dimensionless coded value of the *i*th independent variable, $X_i$ is the experimental value of the *i*th independent variable, $X_o$ is the center point and $\Delta X_i$ is the step change value.

$$N = k^2 + 2k + c_p \tag{1}$$

$$xi = \frac{(Xi - Xo)}{\Delta Xi} \tag{2}$$

The behavior of the model and thereby, the relationship between the independent variables and response is determined by a second-order polynomial function as shown in Eq. (3). In the equation, *Y* is the response that corresponds to reduction (%) of the $CO_2$ concentration measured after each experiment, $b_0$ is a constant coefficient; $b_1$, $b_2$, $b_3$ are linear coefficients; $b_{11}$, $b_{22}$, $b_{33}$ are squared coefficients and $b_{12}$, $b_{23}$, $b_{31}$ are interaction coefficients.

$$\begin{aligned} Y = {} & b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{11}x_1^2 + b_{22}x_2^2 \\ & + b_{33}x_3^2 + b_{12}x_1x_2 + b_{23}x_2x_3 + b_{31}x_3x_1 \end{aligned} \tag{3}$$

Analysis of variance (ANOVA) was carried out to determine the overall significance, probability values, and goodness of fit of the models. Finally, the model was also validated.

## Experimental setup

### Gas-solid carbonation

A stainless-steel reactor that could operate at high process conditions of pressure (up to 100 bar) and temperature (up to 150 °C) was fabricated and used for the study. As comprehended in the literature, fluidized bed reactors (Reddy et al. 2011) and columns (Huntzinger et al. 2009) were reported for conducting gas-solid carbonation. In this study, a stainless-steel reactor of fluidized bed type as shown in Fig. 3a, was employed. The schematic diagram of the study is depicted in Fig. 3b. The maximum operating volume of the reactor is 1 L with a provision at the bottom to place a perforated plate and a Whatman filter paper no. 42, to confine CFA in the reactor. A similar provision is also provided at the top of the reactor. The reactor also consists of a heating unit (round heater and insulation), a digital temperature controller, a temperature sensor, an imported pressure sensor and a digital controller.

### Aqueous carbonation

Aqueous carbonation experiments were carried out in a continuous stirred tank reactor. Based on the studies reported by other researchers (Nyambura et al. 2011; Ji et al. 2019),

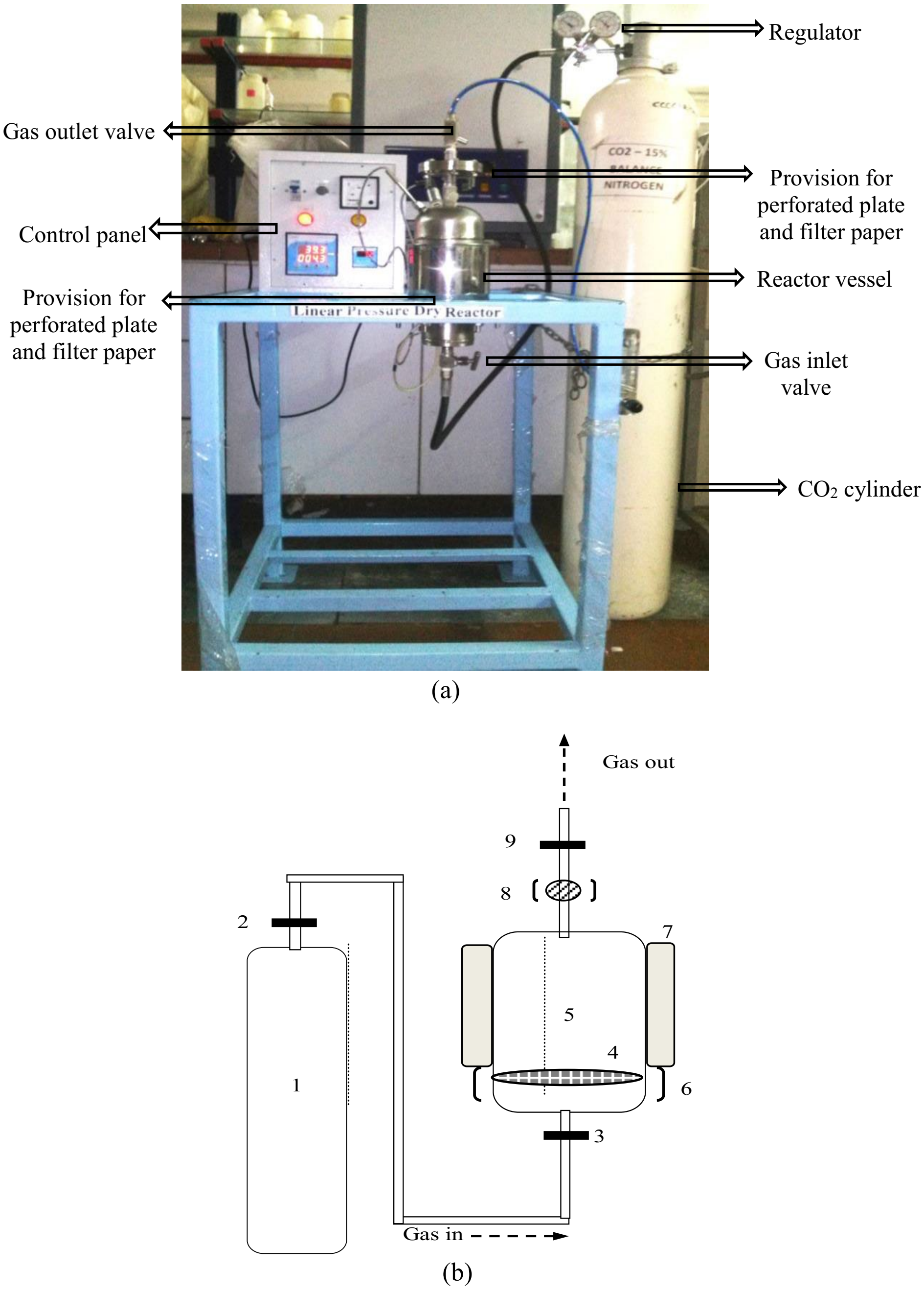
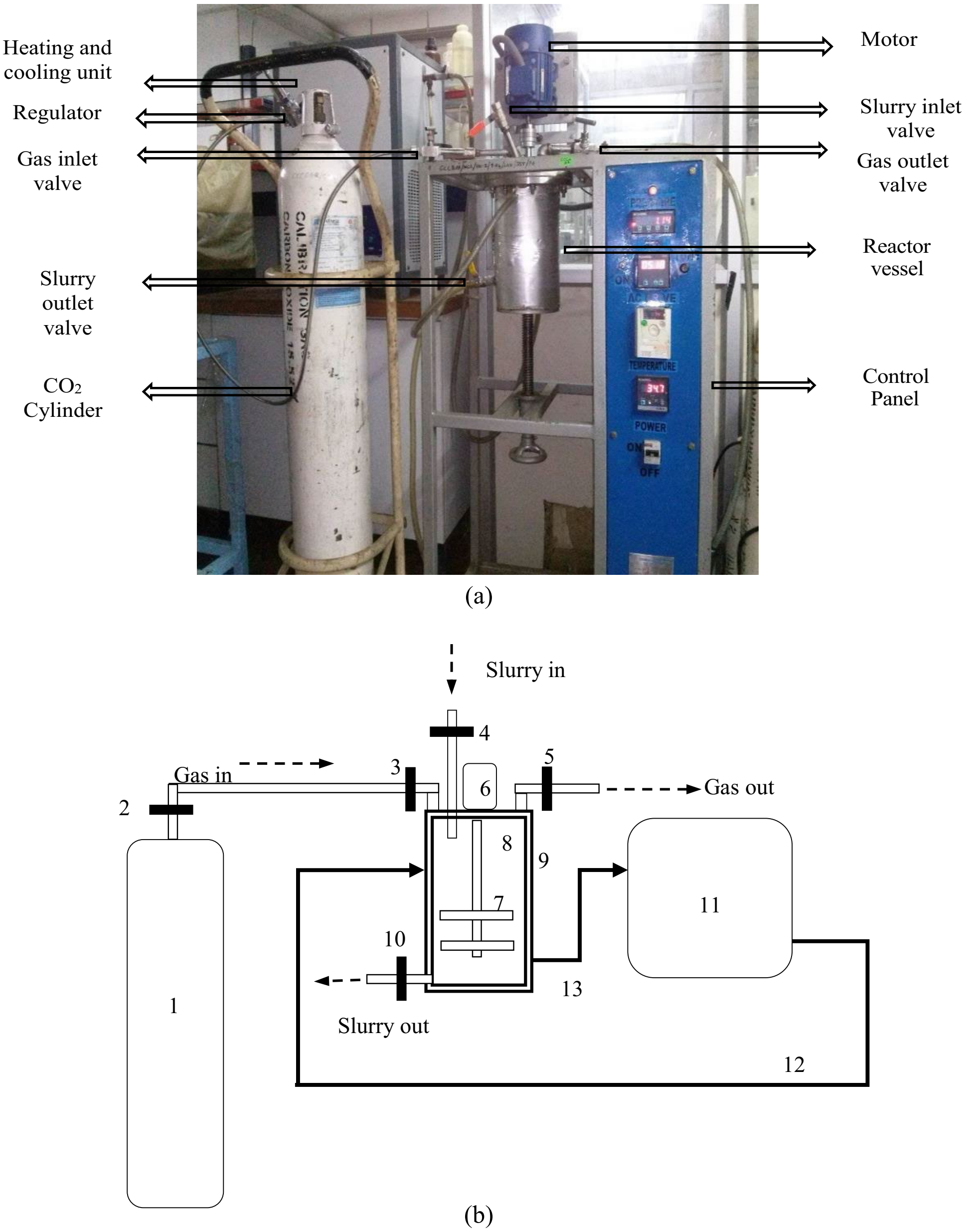


**Fig. 3** **a** Picture and **b** schematic diagram of the experimental set up used for gas–solid carbonation process [1- gas cylinder; 2- high pressure gas regulator; 3- gas inlet valve; 4- perforated plate with filter paper; 5- reactor vessel; 6- provision for placing the waste; 7- heating jacket; 8- provision for perforated plate and filter paper; 9- gas outlet valve]

a continuously stirred tank reactor was designed and fabricated. Figure 4a, b shows the picture and schematic diagram of the reactor, respectively. A stainless-steel reactor (1 L) consisting of four baffles with provisions for slurry inlet at the top and outlet at the bottom was used. The reactor vessel was fitted with a water jacket connected to a heating and cooling unit (inbuilt heater and cooler). The operating range for key parameters, pressure, temperature and stirring speed were 0–100 bar, 30–150 °C and 0–1440 rpm, respectively. The temperature was controlled and monitored using a temperature maintenance setup and digital controller. Pressure gage and controller fitted to the reactor for control and maintenance of pressure inside the reactor. A flame-proof AC motor and an rpm controller provide the stirring effect.

## Carbonation experiments

Gas-solid carbonation experiments were carried out with fresh CFA that being weighed before the experiments. The reactor (Fig. 3) was fastened tightly after placing the waste in it, and then the temperature was increased inside the reactor for each run. After reaching the set temperature value for a



(a)

(b)

**Fig. 4** **a** Picture and **b** schematic diagram of the experimental set up used for aqueous carbonation process [1- gas cylinder; 2- high pressure gas regulator; 3- gas inlet valve; 4- slurry inlet valve; 5- gas outlet valve; 6- motor; 7- stirrer; 8- reactor vessel; 9-water jacket; 10- slurry outlet valve; 11- heating unit; 12- water out; 13- water in]

given run, the reactor was filled with $CO_2$ gas for a predefined value of partial pressure. Experiments were conducted in batches for a time period of 2 h. Gas from the outlet valve was analyzed after the reactor was allowed to return to room temperature. Finally, the reactor was dismantled, and the carbonated CFA was weighed, and then analyzed.

CFA mixed with distilled water for the desired L/S ratio to carry out slurry phase aqueous carbonation experiments. The slurry was then fed into the reactor (Fig. 4), after which the reactor was subjected to heating until it reached the set temperature; Then, the reactor was filled with $CO_2$ gas or until the desired partial pressure value was reached. The carbonation experiment was started by switching on the motor set to provide stirring at 500 rpm. Experiments were conducted for a time period of 1 h. After the experiment, the reactor was cooled to room temperature, and the gas was analyzed for $CO_2$.

All experiments were conducted in triplicates. Effect of reaction time was also studied under optimized conditions of carbonation (both routes).

## Gas analysis

The gas that resulted after each experiment was analyzed using Vaisala CARBOCAP hand-held $CO_2$ meter GM70 with GMP221 probe supplied by Vaisala, India. After each experiment, gas was passed through a rotameter (set value-1 mL/min) followed by the analyzer.

### Carbon analysis of CFA

The carbon content of CFA was determined using total organic carbon (TOC) analyzer. Analytikjena make multi N/C® 2100 S BUTOC analyzer with a solid module HT 1300, Germany was employed for the analysis of the solid product. Calcium carbonate was used for the calibration of the solid module. CFA samples both before and after carbonation experiments were analyzed for carbon, where ever necessary. The samples were analyzed in triplicates. The net carbon gain in CFA calculated from the analysis data was then used to arrive at the sequestration capacity of CFA. The carbonated CFA samples were analyzed as such in the TOC analyzer for gas-solid carbonation experiments. In carbonation studies, the carbonated slurry was filtered using Whatman filter paper no.42. The solid product thus obtained was dried in a hot air oven at 105 °C for 8 h and then taken for carbon analysis.

### Post characterization of CFA

CFA samples after aqueous carbonation under optimized conditions were analyzed to evidence the carbonation process. Fourier-transform-infrared (FT-IR), XRD, and scanning electron microscope (SEM) analyses were performed, and the results were compared with fresh CFA. Bruker Tensor 27 spectrophotometer was used to carry out FT-IR analysis. PANalytical X'pert powder XRD system with Cu $K\alpha$ radiation and 0.02 ° as step size per second was used to find the mineralogy of the carbonated CFA. Carl Zeiss MA15/EVO18 SEM was used to study the surface morphology of the particles.

## Results and discussion

### Gas–solid carbonation

The alkaline metal oxides present in the solid particles of CFA combine with $CO_2$ gas to form solid carbonates under pressurized conditions as indicated in Eq. 4. Eq. 5 shows the reaction of alkaline metal oxide present in a silica matrix with $CO_2$ gas (Bobicki et al. 2012).

$$CaO + CO_2 \rightarrow CaCO_3 \tag{4}$$

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2 \tag{5}$$

Experimental runs as designed by RSM along with the factors (temperature and pressure) and corresponding responses (reduction (%)) are presented in Table 1. The reduction (%) of $CO_2$ was calculated as shown in Eq. 6, where $C_f$ represents the concentration of $CO_2$ gas (%) after the experiment and $C_i$ is the concentration of $CO_2$ gas (%) that was initially fed into the reactor.

$$\text{Reduction (\%)} = \left(\left(C_f - C_i\right)/C_i\right) * 100 \tag{6}$$

Eq. 7 shows the polynomial equation used for the regression modeling, in which $Y$ is the reduction in the concentration of $CO_2$ gas expressed in terms of the factors $x_1$ (temperature) and $x_2$ (pressure).

$$Y = 15.840 + 0.100\,x_1 + 0.002\,x_2 - 0.001\,x_1^2 - 0.001\,x_2^2 - 0.001\,x_1x_2 \tag{7}$$

The results obtained by performing ANOVA on the model are presented in Table 2. $P$-value is the probability of getting an $F$-value, which is a test that compares model variance with residual error. As indicated in the table, $P$-value was found to be very less that is <0.05, thus highlighting the statistical significance of the terms (Grace et al. 2012). Both temperature and pressure were significant, whereas their interaction was insignificant owing to a high $P$-value (0.123). The high $F$-value (107.45) indicates the significance of the regression model for the data. Coefficient of determination ($R^2$) evaluates the fit of the model to the experimental data (Demirel and Kayan 2012). A value of about 0.9874 was obtained showing that the model could explain 98.74% of the variability in the data. Predicted and adjusted $R^2$ values were found to be 0.9456 and 0.9765, respectively. The predicted value suggests that the model can explain 95% of the variability in the new data. Also, $R^2$ and adjusted $R^2$ values were in good correlation demonstrating the high level of correlation between the observed and predicted data. With a

**Table 1** RSM design for gas–solid carbonation of CFA

| Run order | Temperature (°C) | Pressure (bar) | Reduction (%) (experimental) | Reduction (%) (predicted) |
|---|---|---|---|---|
| 1 | 80.00 | 75.00 | 16.60 | 16.53 |
| 2 | 60.00 | 45.00 | 18.00 | 17.88 |
| 3 | 80.00 | 15.00 | 16.79 | 16.66 |
| 4 | 40.00 | 15.00 | 18.30 | 18.13 |
| 5 | 60.00 | 45.00 | 17.80 | 17.88 |
| 6 | 40.00 | 75.00 | 17.76 | 17.65 |
| 7 | 60.00 | 45.00 | 17.92 | 17.88 |
| 8 | 60.00 | 45.00 | 17.93 | 17.88 |
| 9 | 60.00 | 87.42 | 17.25 | 17.33 |
| 10 | 60.00 | 2.57 | 17.62 | 17.78 |
| 11 | 31.72 | 45.00 | 17.70 | 17.85 |
| 12 | 60.00 | 45.00 | 17.84 | 17.88 |
| 13 | 88.28 | 45.00 | 15.92 | 16.01 |
| 14 | 60.00 | 45.00 | 17.76 | 17.88 |

**Table 2** ANOVA results for gas–solid carbonation of CFA

| Source | DF | Seq SS | Adj SS | Adj MS | *F*-value | *P*-value |
|---|---|---|---|---|---|---|
| Regression | 5 | 5.35271 | 5.35271 | 1.07054 | 107.45 | 0.000 |
| Linear | 2 | 3.55984 | 3.55984 | 1.77992 | 178.65 | 0.000 |
| $x_1$ | 1 | 3.36351 | 3.36351 | 3.36351 | 337.59 | 0.000 |
| $x_2$ | 1 | 0.19633 | 0.19633 | 0.19633 | 19.71 | 0.003 |
| Square | 2 | 1.76225 | 1.76225 | 0.88112 | 88.44 | 0.000 |
| $x_1^2$ | 1 | 1.57320 | 1.64866 | 1.64866 | 165.47 | 0.000 |
| $x_2^2$ | 1 | 0.18905 | 0.18905 | 0.18905 | 18.97 | 0.003 |
| Interaction | 1 | 0.03063 | 0.03063 | 0.03063 | 3.07 | 0.123 |
| Residual error | 7 | 0.06974 | 0.06974 | 0.00996 | – | – |
| Lack of fit | 3 | 0.03501 | 0.03501 | 0.01167 | 1.34 | 0.379 |
| Pure error | 4 | 0.03473 | 0.03473 | 0.00868 | – | – |
| Total | 13 | 5.51692 | – | – | – | – |

*DF* degrees of freedom, *Seq SS* sequential sum of squares, *Adj SS* adjacent sum of squares, *Adj MS* adjacent mean square

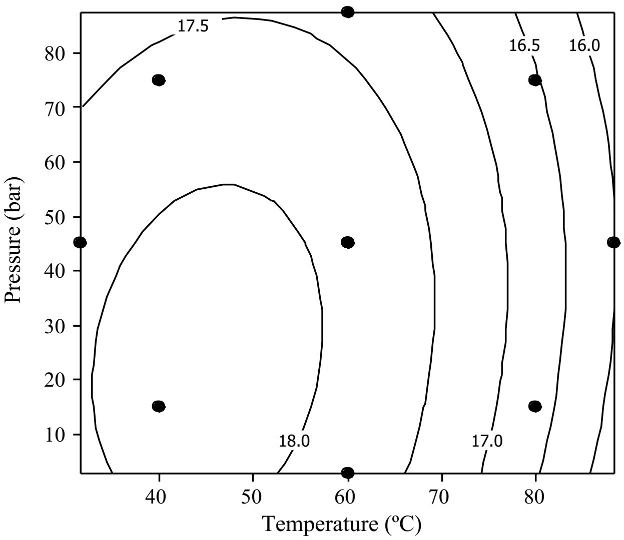


**Fig. 5** Contour plot of reduction (%) for gas–solid carbonation of CFA

*P*-value of >0.05, lack of fit was observed to be insignificant. Thus, it could be summarized that the regression model is statistically significant and good at providing information on the factors and the interaction between them.

Figure 5 shows the contour plot which is a two-dimensional graphical representation of Eq. 4. In other words, the interaction between the factors and their influence on response is depicted in the plot. The global optimum solution for the system obtained using Eq. 7 was found to be at a temperature of 44.86 °C and pressure of 24 bar for a corresponding reduction of 18.2%. The predicted value agreed well with the experimental value (18.14%) under the optimum conditions.

Figure 6 shows the effect of temperature and pressure on the response, namely, reduction (%). The main effect plots indicate that temperature was more significant on the response in comparison with pressure. This means temperature changes will drastically affect the concentration of $CO_2$ gas and hence the carbonation process. This study found the effect of pressure on the carbonation process at high process conditions to be more or less similar to that reported in our previous study (Dananjayan et al. 2016). While, gas-solid carbonation of CFA at room temperature and in varying mild pressure conditions indicated that pressure is a key factor in the process, with this study's findings, it could be inferred that at a given temperature (room temperature), the role played by pressure in the gas-solid carbonation of CFA is profound. However, when both temperature and the pressure were varied, pressure seems to have less significance compared to temperature.

Figure 7 shows the effect of reaction time (0.5, 1, 2, 3, 4, 5 and 6 h) on gas-solid carbonation under optimized experimental conditions of temperature and pressure. Around 3 h of reaction time, the maximum reduction of 20.7 ± 0.8% was achieved, after which there was no considerable progress in the reduction of the concentration of $CO_2$ gas, perhaps due to passivation (Montes-Hernandez et al. 2010). The carbonation process involves a chemical reaction control stage which is usually fast, followed by a slow diffusion control stage. The diffusion of $CO_2$ gas into the CFA particles becomes slower as the reaction progresses due to the dense carbonate layer formed around them (Liu et al. 2018).

## Aqueous carbonation

The alkaline metal oxides present in the solid particles of CFA react with $CO_2$ gas through a set of reactions in the presence of water as shown in Eqs. (8–10). Equation 8 shows the

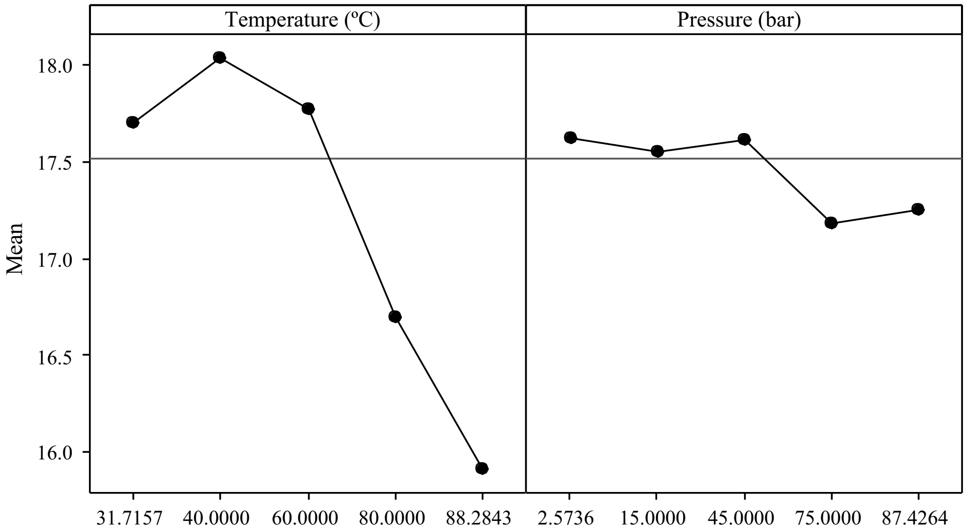


**Fig. 6** Main effect plots of temperature and pressure for gas–solid carbonation of CFA

dissolution of gaseous $CO_2$ molecules in water to form carbonic acid. The carbonic acid thus formed dissociates further to bicarbonates (Eq. 9). Equation 10 shows the further dissociation of bicarbonates to form carbonate ions.

$$H_2O + CO_2 \rightarrow H_2CO_3 \tag{8}$$

$$H_2CO_3 \rightarrow HCO_3^- + H^+ \tag{9}$$

$$HCO_3^- \rightarrow CO_3^{2-} + H^+ \tag{10}$$

Meanwhile, the alkaline metal oxides present in ASR dissolve in water to form hydroxides (Eq. 11). The hydroxide dissociates further (Eq. 12) and finally forms solid carbonates or bicarbonates, shown in Eq. 13 (Bobicki et al. 2012).

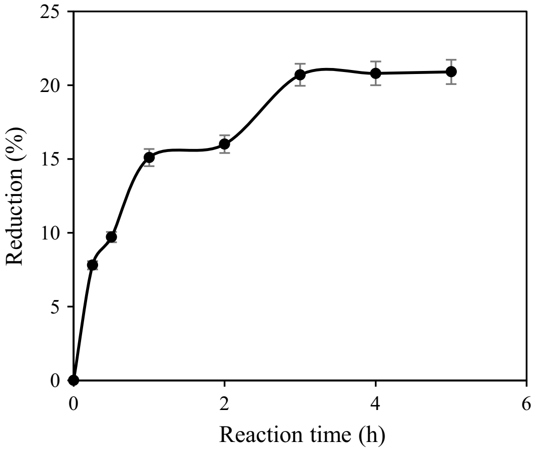


**Fig. 7** Effect of reaction time on reduction (%) for gas–solid carbonation of CFA ($CO_2$ pressure-24 bar, temperature-44.86 °C)

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{11}$$

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \tag{12}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \tag{13}$$

Aqueous carbonation experiments as designed by RSM along with the corresponding response (reduction (%)) for each run are presented in Table 3. The factors included for the slurry phase aqueous carbonation of CFA include temperature, pressure, and L/S ratio. The experiments were carried out for a time period of 1 h. The response, namely, reduction (%) of $CO_2$ gas was calculated as shown in Eq. 6 and fed into the model, which was then analyzed.

Regression modeling was performed using the quadratic equation (Eq. 14), in which, $Y$ is the reduction (%) in the concentration of $CO_2$ (15%) gas, $x_1$ stands for temperature, $x_2$ is pressure, and $x_3$ is the L/S ratio. ANOVA was used to analyze the model, and the results, thus obtained are presented in Table 4. The significance of the model was confirmed by the $P$-value as indicated in the table. It is clear from the table that temperature and the L/S ratio were the most significant factors of the carbonation process, as indicated by the $P$-value. Similarly, the interaction of temperature with pressure and L/S ratio was also significant. $F$-value of 127.25 is less likely to be caused by noise, which shows the significance of the regression model. An $R^2$ value of about 0.9932, indicates that the model could explain 99.32% of the variability in the data set. Moreover, the values of predicted-$R^2$ and adjusted-$R^2$ were determined to be 0.9524 and 0.9838, respectively. Thus, confirming the significance and good performance of the model. From these values, it could be inferred that the regression

**Table 3** RSM design for aqueous carbonation of CFA

| Run order | Temperature (°C) | Pressure (bar) | L/S ratio | Reduction (%) (experimental) | Reduction (%) (predicted) |
|---|---|---|---|---|---|
| 1 | 45.00 | 20.00 | 6 | 19.00 | 18.87 |
| 2 | 45.00 | 70.00 | 20 | 21.90 | 21.68 |
| 3 | 80.00 | 20.00 | 20 | 21.30 | 21.15 |
| 4 | 80.00 | 70.00 | 6 | 20.00 | 19.90 |
| 5 | 62.50 | 45.00 | 13 | 23.10 | 23.10 |
| 6 | 62.50 | 45.00 | 13 | 23.12 | 23.10 |
| 7 | 62.50 | 45.00 | 13 | 23.07 | 23.10 |
| 8 | 91.08 | 45.00 | 13 | 20.52 | 20.79 |
| 9 | 62.50 | 45.00 | 13 | 23.09 | 23.10 |
| 10 | 33.92 | 45.00 | 13 | 20.00 | 20.39 |
| 11 | 62.50 | 4.18 | 13 | 20.20 | 20.50 |
| 12 | 62.50 | 45.00 | 24.43 | 20.50 | 20.92 |
| 13 | 62.50 | 45.00 | 1.57 | 20.40 | 20.64 |
| 14 | 62.50 | 85.83 | 13 | 20.60 | 20.96 |
| 15 | 45.00 | 20.00 | 20 | 19.80 | 19.55 |
| 16 | 62.50 | 45.00 | 13 | 23.14 | 23.10 |
| 17 | 80.00 | 70.00 | 20 | 19.80 | 19.58 |
| 18 | 62.50 | 45.00 | 13 | 23.12 | 23.10 |
| 19 | 80.00 | 20.00 | 6 | 21.60 | 21.47 |
| 20 | 45.00 | 70.00 | 6 | 21.20 | 21.00 |

**Table 4** ANOVA results for aqueous carbonation of CFA

| Source | DF | Seq SS | Adj SS | Adj MS | *F*-value | *P*-value |
|---|---|---|---|---|---|---|
| Regression | 9 | 36.0267 | 36.0267 | 4.0030 | 127.25 | 0.000 |
| Linear | 3 | 0.5631 | 10.5251 | 3.5084 | 111.52 | 0.000 |
| $x_1$ | 1 | 0.2040 | 0.6869 | 0.6869 | 21.84 | 0.002 |
| $x_2$ | 1 | 0.2576 | 0.0413 | 0.0413 | 1.31 | 0.285 |
| $x_3$ | 1 | 0.1015 | 9.7968 | 9.7968 | 311.42 | 0.000 |
| Square | 3 | 28.1187 | 28.1187 | 9.3729 | 297.94 | 0.000 |
| $x_1^2$ | 1 | 9.0529 | 11.6995 | 11.6995 | 371.90 | 0.000 |
| $x_2^2$ | 1 | 9.0699 | 10.4307 | 10.4307 | 331.57 | 0.000 |
| $x_3^2$ | 1 | 9.9958 | 9.9958 | 9.9958 | 317.74 | 0.000 |
| Interaction | 3 | 7.3450 | 7.3450 | 2.4483 | 77.83 | 0.000 |
| $x_1x_2$ | 1 | 6.8450 | 6.8450 | 6.8450 | 217.59 | 0.000 |
| $x_1x_3$ | 1 | 0.5000 | 0.5000 | 0.5000 | 15.89 | 0.004 |
| $x_2x_3$ | 1 | 0.0000 | 0.0000 | 0.0000 | 0.00 | 1.000 |
| Residual error | 8 | 0.2517 | 0.2517 | 0.0315 | – | – |
| Lack of fit | 5 | 0.2511 | 0.2511 | 0.0502 | 251.07 | 0.000 |
| Pure error | 3 | 0.0006 | 0.0006 | 0.0002 | – | – |
| Total | 19 | 36.9612 | – | – | – | – |

*DF* degrees of freedom, *Seq SS* sequential sum of squares, *Adj SS* adjacent sum of squares, *Adj MS* adjacent mean square model was satisfactory in explaining the relationship between the factors and their interaction on reduction (%) in the concentration of $CO_2$ gas.

$$Y = -3.250 + 0.510x_1 + 0.270x_2 + 0.600x_3 - 0.003x_1^2 - 0.001x_2^2 - 0.018x_3^2 - 0.002x_1x_2 - 0.002x_1x_3 + 0.00x_3x_2 \tag{14}$$

Contour plots that graphically represent the regression Eq. (14) used for the modeling of aqueous carbonation are shown in Fig. 8. Interactions between temperature and pressure are shown in Fig. 8a, temperature and L/S ratio in Fig. 8b and, between pressure and L/S ratio in Fig. 8c. The global optimum solution for the system obtained using Eq. (14) was 61.6 °C of temperature, 48.7 bar of pressure and, an L/S ratio of 13.35 for a reduction of 23.1%. Predicted response and experimental response (23.0%) correlated well under optimum conditions.

The effect of the individual factors, namely, temperature, pressure and L/S ratio on reduction (%), are shown in Fig. 9. The plots thus convey the importance of temperature on the carbonation process over pressure and L/S ratio. These plots express the combined effect of three factors on the response. It could be inferred that the most significant factor is temperature, followed by the L/S ratio and then by pressure. Similar results indicating the importance of temperature over pressure in the carbonation of CFA water slurry have also been reported by Montes-Hernandez et al. (2009). Recently, studies have indicated that the carbonation of CFA at a given temperature is dependent on the mineralogy of ASR (Ji et al. 2019). The significance of temperature is associated with its role played in kinetics, equilibrium, dissolution of $CO_2$, and leaching of calcium ions in aqueous carbonation (Pan et al. 2012). According to the Arrhenius equation, an increase in temperature increases the reaction rate constant (Eq. 15). In Eq. 7, $K$ is the reaction rate constant, $T$ is temperature, $R$ is gas constant, and $E_a$ is the activation energy. Thus, as temperature increases, the carbonation process is enhanced up to the optimum value of 61.6 °C. Beyond the optimum value, low reduction (%) values observed at higher temperatures may be per Le-Chatelier's principle which states that increasing temperature decreases the equilibrium constant. In this case, at high temperatures, $CO_2$ gas dissolution decreases even though the rate of leaching of calcium ions increases.

$$K = A \times e^{\frac{-Ea}{RT}} \tag{15}$$

It has been observed that pressure as a factor contributes less to the aqueous carbonation process. Also, its interaction with other factors such as temperature and L/S ratio was least important. Initial $CO_2$ partial pressure plays a significant role in carbonation kinetics by contributing to the

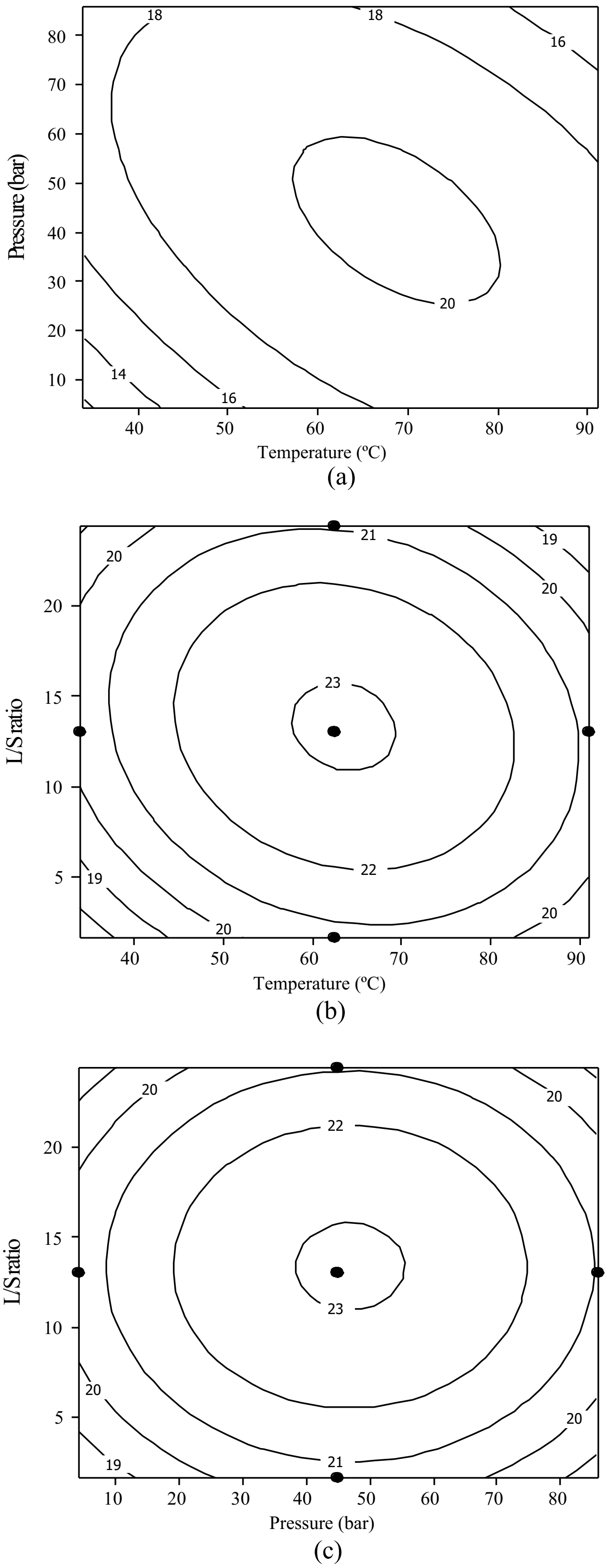


**Fig. 8** Contour plots of the effect of **a** temperature and pressure **b** temperature and L/S ratio **c** pressure and L/S ratio on reduction (%) for aqueous carbonation of CFA

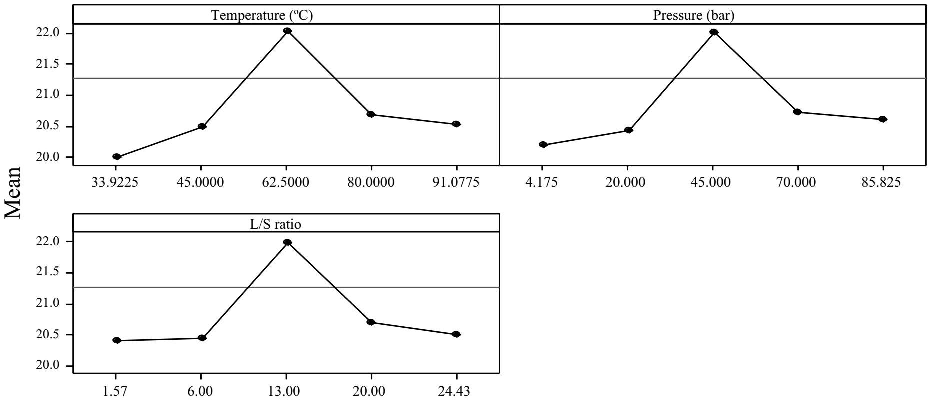


**Fig. 9** Main effect plots of temperature, pressure and L/S ratio for aqueous carbonation of CFA

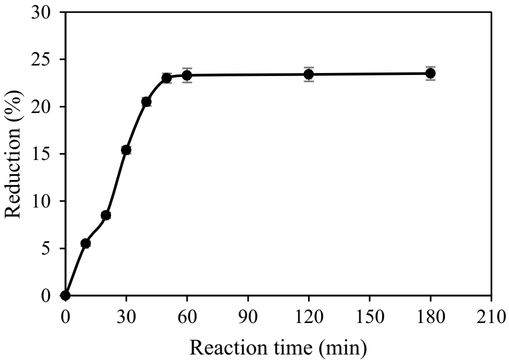


**Fig. 10** Effect of reaction time on reduction (%) for aqueous carbonation of CFA ($CO_2$ pressure-48.7 bar, temperature-61.6 °C, L/S ratio-13.35)

transport of the gas molecules into water. Pressure is insignificant on the extent of carbonation of CFA (Ukwattage et al. 2013). In our previous study, the pressure was found to influence the carbonation process at a given temperature (room temperature) until an equilibrium state was achieved (Dananjayan et al. 2016). This observation highlights that at varying temperatures, the role played by pressure is even less pronounced as it aids only in the kinetics of the carbonation process.

Meanwhile, the significance of the L/S ratio in carbonation of CFA is that an optimum amount of water is needed for the process (Ukwattage et al. 2015). These results are in good agreement with the results obtained in our previous study (Dananjayan et al. 2016), wherein the L/S ratio played a significant role in the carbonation process at a given temperature. The significance of water content in the carbonation process can be reasoned on the requirement of water for the diffusion of gas molecules, dissolution and transportation of alkaline oxides of CFA, and for the hindrance created by the carbonate layer (Liu et al. 2018).

Fig. 10 presents the results obtained by varying reaction time on the aqueous carbonation of CFA. In aqueous conditions, carbonation of CFA was quite fast and, the maximum reduction (23.0 ± 0.7%) in the concentration of $CO_2$ gas was attained within 50 min. An increase in the reaction time beyond the optimum value resulted in a stagnant state due to passivation. Passivation is caused by the carbonate layer formed on the CFA particles (Nyambura et al. 2011). Water has a positive impact on both the chemical reaction stage and the diffusion control stage by promoting the formation of hydroxides of calcium during the carbonation process (Liu et al. 2018).

**Table 5** CE of CFA

| Carbonation route | Actual sequestration capacity (g of $CO_2$/kg of CFA) | CE (%) |
|---|---|---|
| Gas-solid | 21.03 | 28.4 |
| Aqueous | 50.72 | 68.5 |

The result thus obtained (reduction-23%) is comparable with the laboratory study conducted with CFA and flue gas ($CO_2$-13%) by Reddy et al. (2011) in which a reduction of 26.2% was reported. The temperature used in the study was in the range of 43–54 °C and pressure between 0.88 and 1.14 bar with the maximum reduction occurring within 2 min. Though the reduction (%) is similar for both studies, it should be noted that the particle size of CFA was 40 µm in the older study, while it is < 700 µm in the present study. This comparison highlights the importance of particle size in the carbonation process. The influence of particle size on the carbonation process and its interaction with other factors especially, pressure and L/S ratio, can be inferred.

## Carbonation efficiency (CE)

The theoretical sequestration capacity of CFA calculated using Stenoir's stoichiometric formula is 7.41%. In other words, 1 kg of CFA can capture 74 g of $CO_2$. CE of CFA in gas-solid, as well as aqueous carbonation process, was calculated (Eq. 16) and the results are presented in Table 5.

The inference from the results is that slurry phase aqueous carbonation is the most suitable for CFA with a maximum sequestration capacity of 50.72 g of $CO_2$/kg.

$$\text{CE} = (\text{Actual sequestration capacity}/\text{theoretical sequestration capacity}) \times 100 \tag{16}$$

The result obtained in the aqueous route was superior to that reported by Montes-Hernandez et al. (2009), in which maximum sequestration of 26 g of $CO_2$/kg of CFA (CE-82%) was attained through slurry phase aqueous carbonation. The results in this study indicated that carbonation of CFA in the gas-solid route was also comparable with the result obtained by Montes-Hernandez et al. (2009), as the sequestration capacity is almost the same. This observation may be because, in this study, CFA contained a high content of calcium oxide (6.74%) than that used by them (CaO-4.1%).

CE attained by slurry phase aqueous carbonation of CFA in this study (68.5%) was much higher than that obtained by Ukwattage et al. (2015). Ukwattage et al. (2015) studied wet phase aqueous carbonation of CFA with water, and the maximum CE was 10.9–13.9%, which was attained at 60 °C with an L/S ratio of 0.2–0.3. The wet phase mode of aqueous carbonation attempted by them may be the reason behind the large gap in CE as the significance of water in the carbonation of CFA has already been discussed in the previous section.

Ji et al. (2019) achieved 80% CE of CFA through aqueous carbonation and pure $CO_2$ gas at 220 °C with a sequestration capacity of 132 g of $CO_2$/kg of CFA. The high values reported may be attributed to the high quantity of alkaline oxides (> 60%), use of high temperature (40–220 °C) conditions, and carbonation with pure (100%) $CO_2$ gas.

The results obtained in gas-solid carbonation of CFA are comparable with those reported by Altiner (2018) whose study determined the carbonation potential of five different Turkish fly ashes at ambient temperature and pure $CO_2$ gas with mild conditions of pressure (1–5 bar). A wide range of sequestration capacities was reported depending on the alkalinity and mineralogy of CFA. Sequestration capacity ranged from 1.3 to 72 g $CO_2$/kg of CFA. Maximum CE of about 53% of CE was achieved with a CFA whose CaO content was 20%.

Cwik et al. (2018) also performed gas-solid carbonation of CFA which had a high calcium content of about 35% with pure $CO_2$ gas. They achieved a maximum sequestration capacity of 117.7 g of $CO_2$/kg of CFA at 160 °C and 1 bar of $CO_2$ pressure with a CE of 48%. Though the sequestration capacity attained in that study was much higher than what is reported in this study owing to the high content of alkaline oxides in the waste used by the former, the present study gives an improved CE value (68.5%) as compared to 48% achieved by the older study. It has to be noted that they have used pure (100%) $CO_2$ gas which may also be the reason behind observed high sequestration capacities. The lower CE achieved by them may be due to the selection of the carbonation process route.

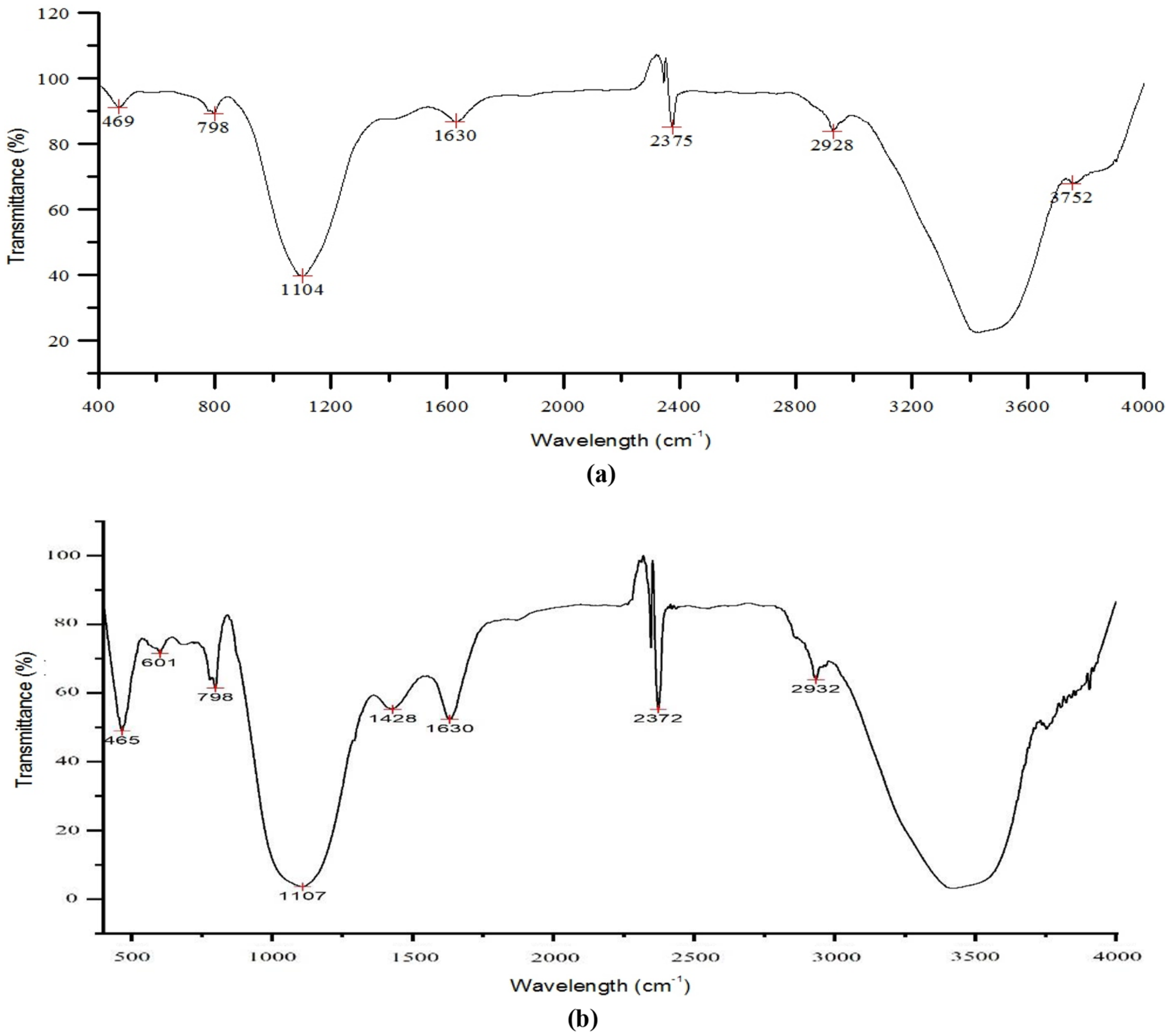
CE (28.4%) attained using gas-solid carbonation of CFA is comparable with that reported by Liu et al. (2018). They conducted fixed bed carbonation of CFA (CaO-28%) with and without steam addition. A maximum CE of 28.74% was achieved at 600 °C, 1 bar with 20% steam addition. Though the sequestration capacity is much higher i.e., 60 g of $CO_2$/kg of CFA, than reported in this study, CE is lower due to the choice of the carbonation process. It should be noted that the researchers inferred that steam addition aids the carbonation process suggesting the influence of water in the system.

The results and comparison with other reported studies suggest that the sequestration capacity of CFA is highly dependent on its composition, especially its CaO content. Whereas, CE depends on the choice of carbonation route. The slurry phase aqueous carbonation process is more suitable for CCS using CFA than wet phase aqueous carbonation and gas-solid carbonation in the process conditions studied.

## Mass balance calculation

$CO_2$ captured under optimal conditions was considered for the calculation purpose. The experiment of CFA under an aqueous carbonation route (temperature-61.6 °C, pressure-48.7 bar, L/S ratio-13.35, reaction time-50 min, reduction-23.1%) that yielded a maximum sequestration capacity of 50.72 g of $CO_2$/kg of CFA was subjected to mass balance calculation. The amount (moles) of $CO_2$ absorbed in the reactor was determined using ideal gas law as shown in Eq. 8 (Montes-Hernandez et al. 2009). In Eq. 17, $P$ is the pressure drop observed in the reactor (0.5 bar), $V$ is the volume occupied by the gas (0.46 L), $T$ is the temperature used in the study (334.75 K), and $R$ is gas constant (0.08314472 L bar/K mol). Thus, the amount of $CO_2$ absorbed in the reactor is calculated to be 4.2 moles using Eq. 17. To establish the mass balance, the net carbon content of the carbonated CFA obtained at optimum conditions of the carbonation experiment was analyzed using TOC analyzer. CFA was found to have a net carbon gain of 185.4 g/kg (4.2 moles) as a result of carbonation. Hence, it could be inferred that the values are in good agreement.

$$n = PV/RT \tag{17}$$



(a)

(b)

**Fig. 11** FT-IR spectra of CFA **a** before carbonation **b** after aqueous carbonation

## Characterization studies

Fresh CFA was found to be with a pH of 9.41, ANC of 0.07 meq/g and EC of 2.84 mS/cm. CFA after gas-solid carbonation exhibited a pH of 8.5, ANC of 0.06 meq/g and EC of 2.6 mS/cm. The values of pH, ANC and EC further decreased after aqueous carbonation which was about 7.7, 0.05 meq/g and 2.03 mS/cm, respectively. The trend shows that the carbonation process has reduced the alkalinity of CFA (Johnston et al. 2010).

FT-IR spectra of fresh CFA (Fig. 11a) indicated the presence of the OH group (3200–3600 cm$^{-1}$). The Si–O bands in both fresh CFA (Fig. 11a) at 469 cm$^{-1}$ and carbonated CFA (Fig. 11b) at 465 cm$^{-1}$ confirm the presence of silica, a major component of CFA. FT-IR spectra of carbonated CFA (Fig. 11 b) indicated the formation of calcium carbonate as established by the presence of peaks in the region of 1400 and 800 cm$^{-1}$ due to aqueous carbonation.

Mineralogy of fresh and carbonated CFA was found using XRD analysis and is shown in Fig. 12a, b, respectively. Both fresh and carbonated CFA were composed of mineral phases such as mullite, quartz, hematite, magnetite, periclase and anhydrite. Fresh CFA exhibited peaks of lime which were found to be absent in the carbonated CFA. Peaks of calcite were prominent in the carbonated CFA.

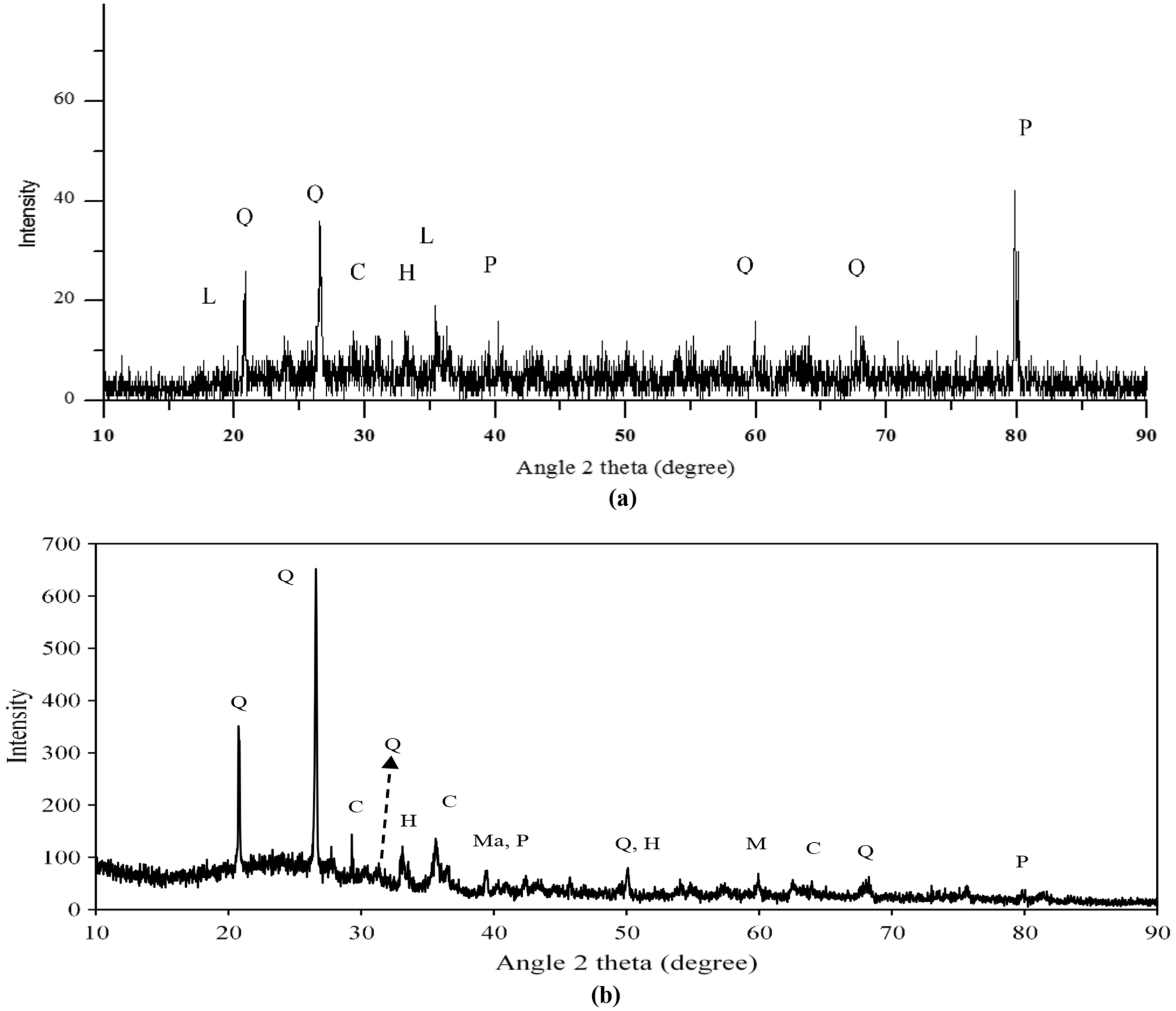


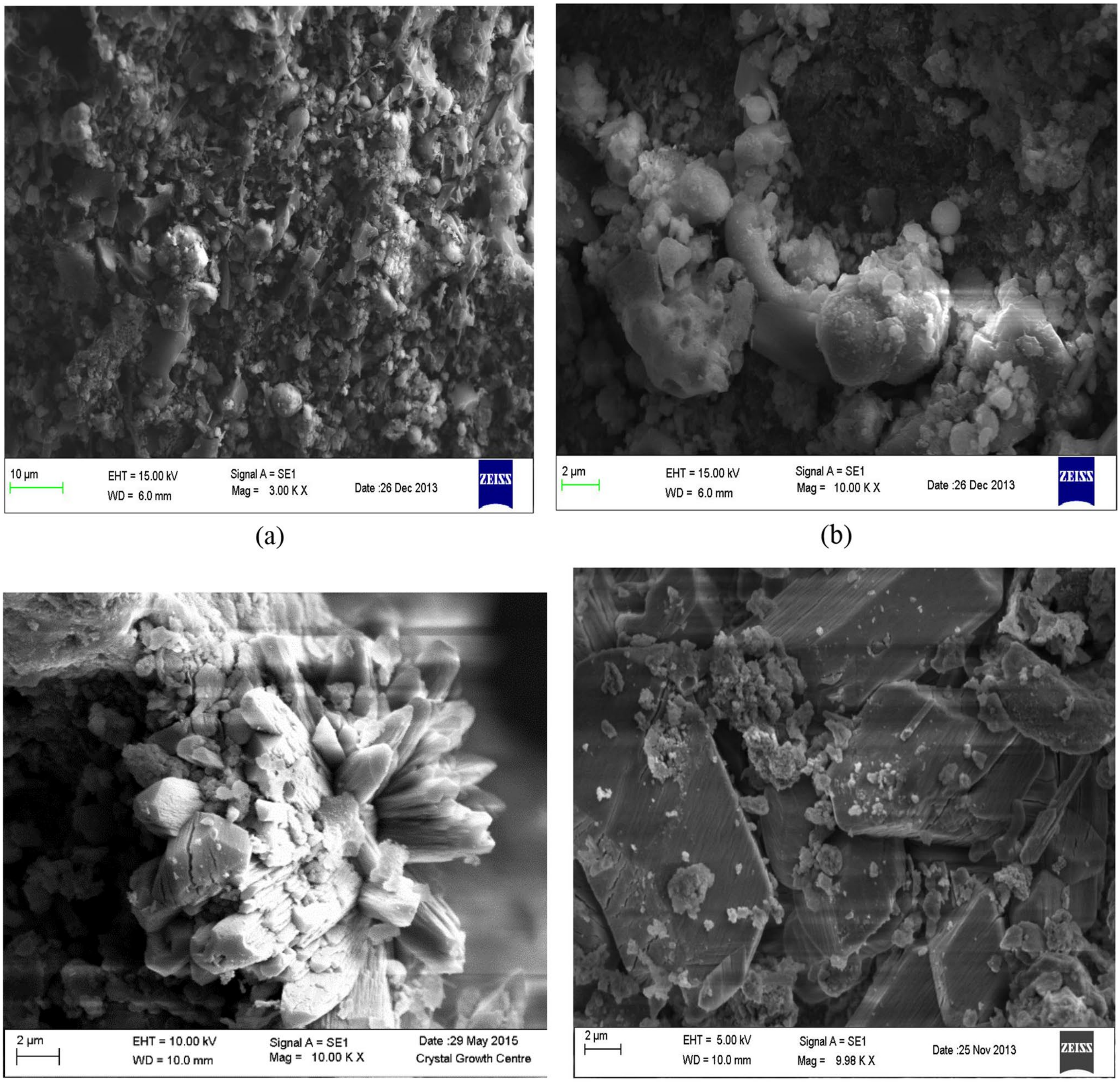
**Fig. 12** XRD spectra of CFA **a** fresh **b** after aqueous carbonation at high process conditions [Q-quartz ($SiO_2$), L- lime (CaO), C-calcite ($CaCO_3$), A- anhydrite ($CaSO_4$), H-hematite ($Fe_2O_3$), Ma-magnetite ($Fe_3O_4$), P- periclase (MgO), M-mullite ($Al_2O_3SiO_2$),]

Fresh CFA and carbonated CFA were examined using SEM to study the morphology of the particles. The images are presented in Fig. 13a–d. CFA particles are typically cenospheres as seen in Fig. 13a, b. The formation of calcite is evidenced by the presence of cubic structures in the CFA particles after wet carbonation (Fig. 13c, d).

## Carbonation potential and future prospects

India's annual production of CFA is about 217 t, and if it is utilized for CCS, about 11 t of $CO_2$/y could be sequestered with the current process. If further process development and improvement of the carbonation process is carried out to achieve the entire carbonation potential (74 g of $CO_2$/ kg) of CFA, and then about 26 t of $CO_2$ could be sequestered per year by CFA.

India emits 1077.4 $tCO_2e$/y from its energy sector (USAID 2018). If we consider that 70.72% of net greenhouse gas emission in India is contributed by $CO_2$ as per the estimates by INCCA (2010) the $CO_2$ emissions per year will be 754.2 t. In that case, the carbonation potential of Indian CFA would be 1.5% and 3.5%, corresponding to the CE of 68.5% and 100%, respectively. Thus, the impact of this technology would be minimal if the current process is implemented as such in power plants. Further development



(a) (b) (c) (d)

**Fig. 13** SEM images of CFA **a** & **b** fresh **c** & **d** after aqueous carbonation at high process conditions

of the carbonation process is required to witness appreciable results at the large-scale implementation of the technology.

## Conclusion

Coal fly ash is an alkaline solid residue that is available at proximity to coal-fired power plants, one of the major point source emitters of $CO_2$, thereby providing a major cost-benefit to the application of carbon capture and storage. The present study is representative of Indian fly ashes that mostly belong to class F type. This study emphasizes the utilization of CFA toward the emergence of a clean solution to carbon capture and storage in the country, wherein, other options, namely geological and ocean storage are not likely feasible due to the high cost and energy requirements. This laboratory-scale study of coal fly ash with flue gas at high process conditions has demonstrated the likelihood of using ASR for carbon capture and storage technology. Herein, a maximum of about 23% of reduction in the concentration of $CO_2$ present in the flue gas was observed due to the carbonation process. Among the two process routes, aqueous carbonation of the waste yielded maximum carbonation efficiency of 68.5% with the temperature being the most influential factor. While Indian coal fly ash could be a suitable candidate for CCS, its carbonation potential and efficiency need improvement for large-scale implementation of the process.

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## Declarations

**Conflict of interest** The authors declare that they have no conflict of interest.

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