Experimental Investigation of CO_2 Sequestration in Fly Ash and Lime Composites via Mineral Carbonation: A Lab-Scale Study

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Abstract. CO_2 emissions are widely acknowledged as the main factor behind the rapid increase in global temperatures, resulting in substantial changes to climate system. Emissions and waste from thermal power plants pose a serious environmental concern. This study aims to explore the cost-effective bulk utilization of fly ash for CO_2 sequestration. The fly ash and hydrated lime was mixed in varying proportions and tested for CO_2 sequestration, compressive strength, consistency, and free water content as a function of CO_2 mixing rate and injection pressure. Coal fly ash and hydrated lime composition with 4% (wt.) lime resulted in an impressive compression strength of 1.7 MPa and a CO_2 absorption of 5.4%.

Keywords: CO_2 sequestration, mineral carbonation, Fly ash & Concrete

1 Introduction

Anthropogenic carbon dioxide emissions are widely acknowledged as the primary catalyst for the accelerated rise in global temperatures during the past six decades, resulting in profound transformations of universal climate framework[1].Carbon capture and storage (CCS) may be substantially feasible as a strategy to abate the environmental impact of carbon dioxide emissions [2]. Mineral carbonation, Carbon dioxide capture through alkaline earth mineral reactions such as alkaline earth metal oxides or hydroxides, presents an attractive approach within the realm of CCS, potentially utilizing natural resources and industrial byproducts [3]. Silicate minerals enriched in calcium oxide or magnesium oxide, along with industrial waste products including steel slag, Coal Fly Ash (CFA), Coal Bottom Ash (CBA), bauxite residues, concrete waste, and municipal solid waste incineration residues, may be employed as raw materials for the mineral sequestration of carbon dioxide [4–7]. Despite having a relatively low content of free calcium oxide, CFA shows significant potential for mineral carbonation due to its large production volume [8]. Exceeding 800 million tons annually, CFA constitutes a substantial global byproduct. As Coal-fueled power station are major driver of global warming, contributing nearly 40% of greenhouse gas discharge, the on-site sequestration of CO_2 within these power plants using CFA can contribute to a substantial reduction in global CO_2 emissions [9]. Additionally, this

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approach has the potential to reduce both the expense and discharge associated with transporting CFA to landfills [10].

CFA possessing specific compositional characteristics finds broad application in the construction industry as an admixture [11,12]. Moreover, there exist methodologies for synthesizing materials such as zeolites and adsorbents from CFA, thereby expanding its potential utility for diverse purposes [13]. CFA isn't being used as much as it could be in practical situations around the world.

Massive quantities of coal fly ash are needlessly dumped in landfills and ash ponds, leading to severe environmental problems such groundwater contamination and degradation, spreading to natural areas, and deteriorating air quality [14]. Consequently, a significant increase in CFA utilization rates could provide a viable strategy for mitigating this environmental impact. The elevated CaO and MgO content in CFA can induce expansive reactions in construction materials, limiting its use in cement and concrete[15,16]. Sequestering CO_2 with CFA is a great way to reduce greenhouse gases and help manage the environmental problems caused by CFA. Utilizing CFA with lower CaO and MgO content can enhance its potential for application[17].The mineral carbonation process can be conducted in both moist and dry environments. However, the dry method, though simpler, faces challenges due to its sluggish reaction rate and limited CO_2 sequestration capacity, whereas wet carbonation demonstrates enhances CO_2 sequestration [18]. There are two approaches to wet carbonation: direct and indirect. The direct method transforms fly ash and carbonation products into solid, reusable material for construction or landfill disposal. In direct carbonation, fly ash reacts with CO_2 in an aqueous environment, forming carbonates through the reaction of carbonic acid with alkaline constituents [19]. Whereas in indirect carbonation, reactive components like calcium are first leached into a solution, and then react with CO_2 to form carbonates, offering better control over the final product. However, indirect carbonation is time and capital consuming. The direct method of carbonation offers the benefits of simplicity and reduced chemical use, making it the preferred technology for CO_2 mineralization using fly ash. The fundamental reaction in this process is the direct carbonation of fly ash with gaseous CO_2. Further, the limited calcium oxide (CaO) content in class F fly ash can hinder CO_2 sequestration. The interaction between fly ash, lime, and water under high pressure and temperature leads to hydration reactions, forming calcium silicate hydrates (CSH) and calcium aluminate hydrates (CAH). These compounds contribute to the development of high strength and durability. Hence, his research seeks to unlock the potential of CFA lime slurry for effective CO_2 capture by investigating the effects of temperature and pressure.

2 Materials & Method

2.1 Materials

The Coal Fly Ash-F (CFA-F) and Hydrated Lime (HL) were received from NTPC Ramagundam and Akshar chemical Mumbai with 90% purity, respectively. The CO_2 for the study was procured from Star Special Air with 99.99% purity. All the samples were prepared with normal water at ambient condition.

2.2 Methods

2.2.1 Particle Size Distributions

The particle size analysis was performed using Malvern Mastersizer HYDRO 2000MU. The fly ash sample was dried in oven at 105 °C for 24 hrs prior to analysis. The analysis was performed via wet analysis method, where sample was added to a dispersing medium (Deionized water) and ultra-sonicated for finer dispersion.

2.2.2 Elemental composition

Elemental analysis of CFA-F/HL was conducted using Energy-Dispersive X-ray Fluorescence (ED-XRF) spectroscopy (EX-6600 model, Xenemetrix). The sample was analyzed in its powder form. The spectrum was collected in the energy range 10 to 40 keV.

2.2.3 Slurry Preparation and CO_2 Purging

Table 1 outlines the various dosages of CFA-F, HL, and water that were mixed in different proportions to prepare the slurry. To sequester CO_2 within the slurry, CO_2 gas was purged during the stirring process as shown in Fig1. A 1 L PET (polyethylene terephthalate) trough was used to sequester CO_2 within the slurry. The trough was then sealed airtight, and the air was flushed out through an outlet port by CO_2 purging). Furthermore, the CO_2 injection pressure was controlled using a pressure regulator attached to the cylinder.

2.2.4 Effect of Solid- liquid ratio, stirring rate on CO_2 sequestration

CFA-F/HL slurries, prepared according to the specifications in Table 1, were exposed to varying CO_2 injection pressures ranging from 0.5 to 2 bar. The CFA-F/HL slurries were progressively agitated, achieving a fully homogeneous mix after 5 minutes of stirring. After 5-minute agitation, the slurries were allowed to dry at ambient conditions (atmospheric temperature ~25 °C, humidity ~20%, air pressure ~ 1 bar) for 24 hours. The dried samples were then crushed and analysed using STA to quantify CO_2 release. CO_2 sequestration by different CFA-F/HL slurries was measured at various range of injection pressure and rpm. Additionally, the influence of stirring rate on CO_2 sequestration was also investigated.

Table 1. Dosage of CFA-F, HL and Water

S. No	CFA-F	HL	Water	Sample
1	100%	0%	20%	S0
2	99%	1%	20%	S1
3	98%	2%	20%	S2
4	97%	3%	20%	S3
5	96%	4%	20%	S4
6	95%	5%	39%	S5
7	90%	10%	39%	S10

*CFA-F and HL together indicates 100% of solid material in all rows .water is added by weight of solid i.e flyash +lime.

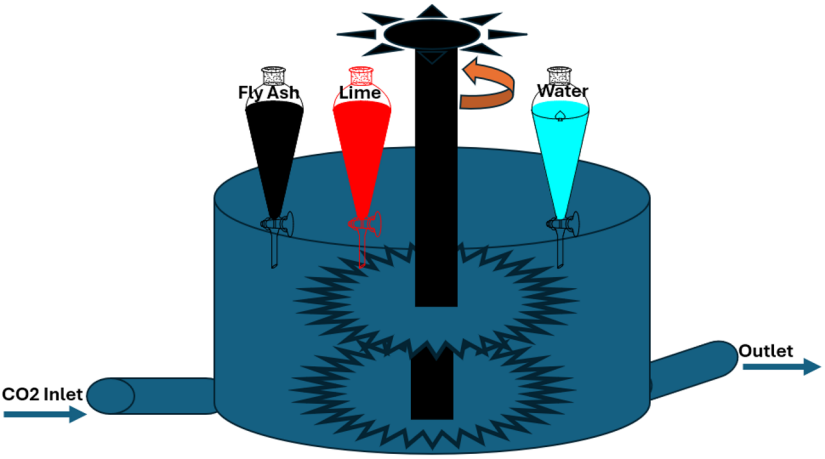

Fig. 1. Schematic for CO_2 purging setup

2.2.5 Measurement of CO_2 sequestration

The CO_2 sequestration in the CFA-F/HL slurry was evaluated through a Simultaneous Thermal Analyzer (STA 449 F1 JUPITER, NETZSCH), which integrates TGA and DSC techniques to analyse the thermal behaviour of materials and track mass changes, including CO_2 release during decomposition. After drying the CFA-F/HL slurry in a heated air oven at 40°C, the sample was crushed using a pulveriser. 10 milligrams of the crushed sample were then placed in the STA, where mass loss was recorded over time (Fig3). The STA was operated with temperature ramp rate of 30°C/min, form 40°C to 1000 °C with N_2 gas flow rate of 30 mL/min. The mass loss calculated from STA was plotted as a function of pressure and rpm.

2.2.6 Scanning Electron Microscope (SEM) Imaging for carbonate deposit

Scanning electron microscopy (SEM) (FEI Quanta 200, ThermoFisher Scientific, New Delhi, India) was employed to analyse the morphologies of CFA-F, HA, and the carbonate deposits formed due to CO_2 sequestration.

2.2.7 Consistency of Fly Ash Lime slurry

The Consistency of the slurry influences CO_2 diffusion within the mixture. If the slurry is too thick, gas penetration may be restricted, slowing carbonation. If too thin, CO_2 may escape before sufficient reaction with lime, reducing carbonate formation efficiency. The flow behaviour of the CFA-F/HL slurry, prepared as per Table 1, was studied using an atmospheric consistometer (Model 200, CTE, Tulsa, Oklahoma, USA). The various CFA-F/HL slurries were poured into the consistometer cup, which was equipped with a paddle and potentiometer. During the consistency test, the slurry cup maintained a constant rotation at 150 rpm, while the paddle gradually began rotating as the CFA-F/HL slurries hardened. As hardening progressed, the potentiometer coil twisted, generating torque. This torque, resulting from the slurry's hardening, was recorded as consistency and measured in Bearden units of consistency (Bc).

2.2.8 Cube Casting & Compressive Strength

The CFA-F/HL slurry, following CO_2 dosing, was poured into a cube mold measuring 70.5 × 70.5 × 70.5 mm^3. The cubes were allowed to dry in ambient conditions (atmospheric temperature ~25 °C, humidity ~20%, air pressure ~ 1 bar) for 24 hrs. Then, the cubes were subjected to compressive strength testing using Enkay 2000N compression testing machine as shown in Fig2.

Fig. 2. Cube Cast from S1 to S4 before and after CO_2 sequestration (a) and Enkay 2000N compression testing machine (a).

2.2.9 Assessment of free water in fly ash-lime slurry

Free water in cement and concrete is the excess water that isn't chemically bound to the cement particles. It significantly affects the strength, durability, and workability of concrete. The free water was determined using gravimetric method. To measure free water, a concrete cube was weighed (M1) before and after drying (M2) it in an oven at (105-110) ℃. The difference in weight % represents the amount of free water M.

$$\%\,\text{Free Water M} = \frac{(M_1 - M_2)}{M_1} \times 100 \tag{1}$$

3 Results and Discussion

3.1 Particle Size Analysis

The analysis of particle was done to measure the spread of CFA-F particles is presented as Fig3. Majority of the particles fall in the range of 100 µm, whereas approximately 30-40% particles are also observed in the range of 10 µm. Smaller particle size renders higher specific surface area which enhances the reactivity of particle with hydrated lime. This enhances reactivity further improves the durability of the fly ash lime composite. Additionally, smaller particles instigate micro porosity in the composite. This micro porosity improves absorption of CO_2 in to the composite.

3.2 Energy Dispersive X-ray Fluorescence (EDXRF)

The elemental composition of CFA-F and HL is presented in Table-2. Among the various oxides present in the CFA-F and HL. The EDXRF results of fly confirm the typical class F fly ash composition with low Ca and Mg content. The hydrated lime showed high amount of CaO of about 73.1%. Apart from Ca, other elements observed in the composition were of trivial level.

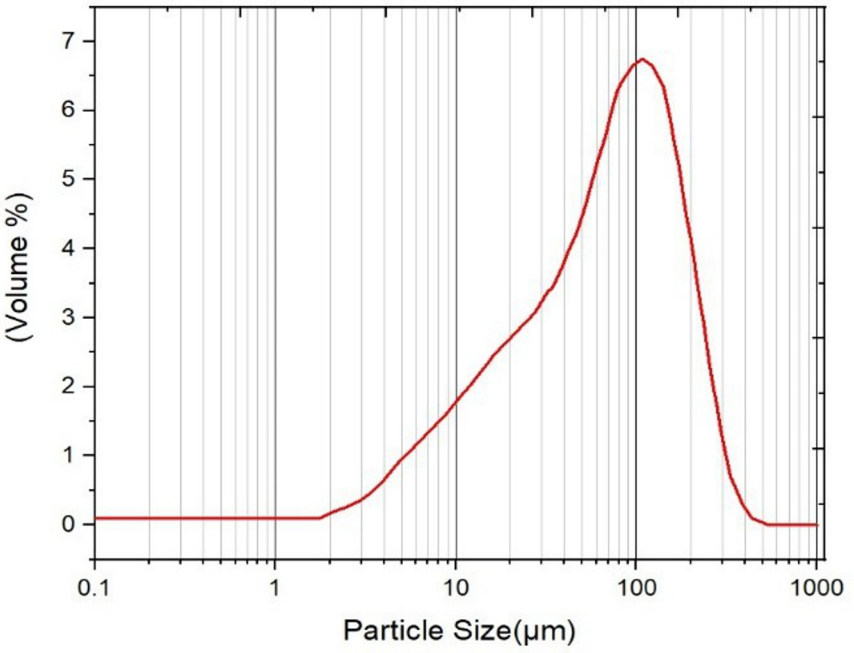

Fig. 3. Particle Size distribution of coal fly ash.

Table 2. Elemental Composition of Fly ash and Hydrate lime

Sample	CFA-F	HL
Na_2O	0.15	0.188
MgO	0.94	0.06
Al_2O_3	26.52	0.22
SiO_2	60.64	0.49
P_2O_5	0.18	0
SO_3	0.13	0.33
K_2O	1.51	0.14
CaO	1.19	73.16
TiO_2	2.02	0.02
MnO	0.032	0.01
Fe_2O_3	5.8	0.06

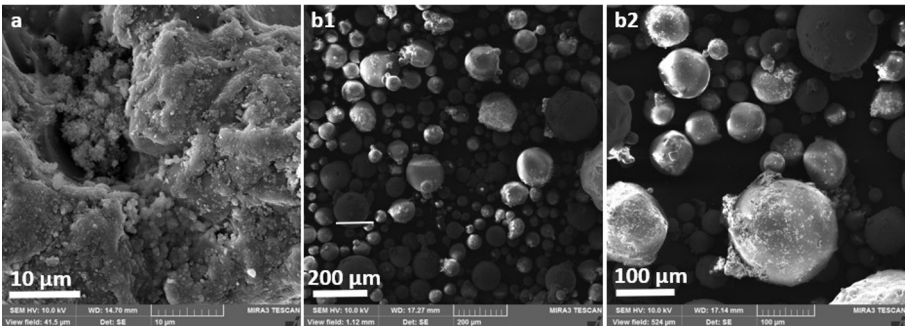

Fig. 4. SEM Images of (a) Hydrated Lime and (b1, b2) Coal Fly Ash.

3.3 SEM Analysis of CFA-F/HL slurry after carbonation

The SEM analysis Fig 4 (a) shows the irregular texture and morphology of calcium hydroxide flakes present in hydrated lime. In contrast, Fig 4(b1) displays the regular spherical geometry typical of CFA-F particles. Upon further magnification Fig 4(b2), the CFA-F particles exhibit a clear, rounded structure with particle size less than 200 µm. In an aqueous slurry phase, the spherical morphology of particles typically hinders gas diffusion. However, this slower diffusion rate can increase the contact time between CO_2 and lime particles, promoting carbonate formation in the slurry [20].

3.4 Effect of solid-liquid ratio, stirring rate on CO_2 sequestration

The resulting mass loss (due to $CaCO_3$ decomposition indicating CO_2 Sequestered) percentages were plotted against mixing rate at 1 bar in the Fig 5(a). The CO_2 sequestration percentage increases slightly up to 300 RPM. There was no significant increase in mass loss observed with further increase in mixing rate. However, the injection pressure significantly affected the mass loss observed. The CO_2 sequestration increases with increase in injection pressure up to 1.5 bar, as shown in Fig 5(b). There was no further mass loss observed beyond 1.5 bar. This is due to reason that CO_2 absorption is directly proportional to the lime content in the composite. CO_2 is trapped in the composited in the form carbonates of calcium. The mass loss is observed in Simultaneous Thermal Analyzer (STA) due to thermal decomposition of these carbonates at around 680 °C [20].

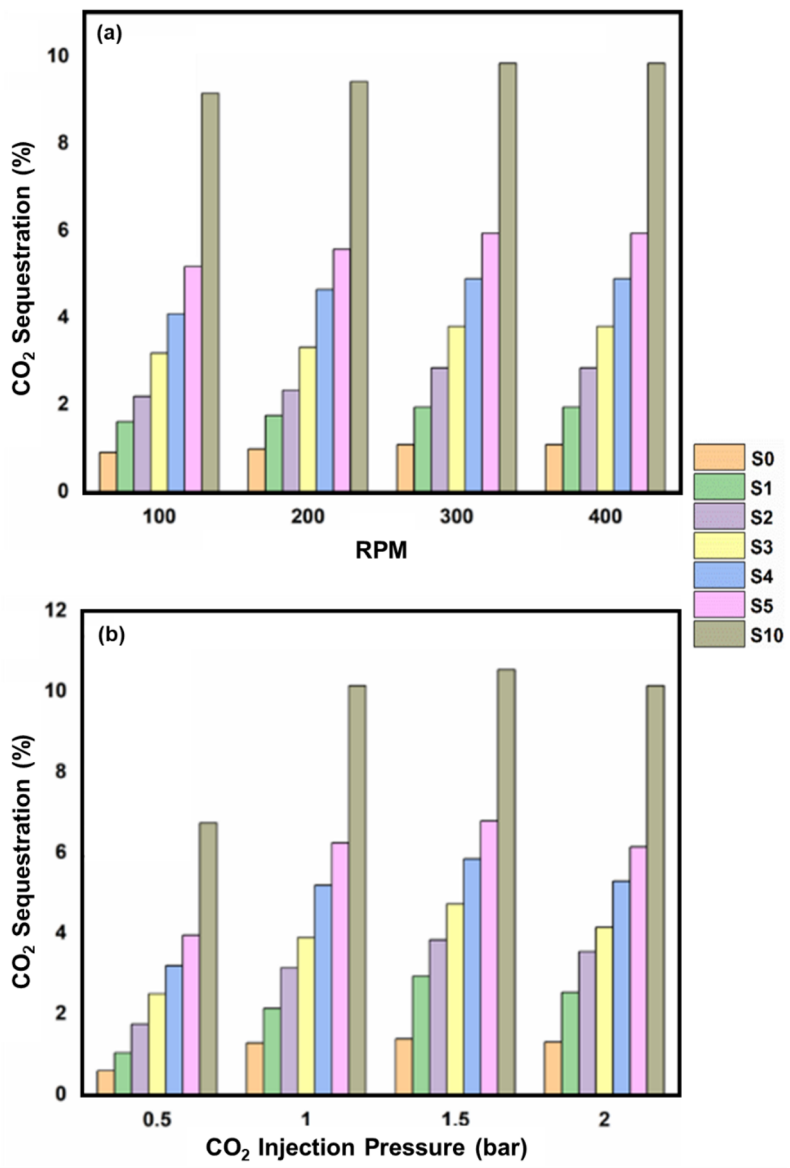

Fig. 5 Plots showing **(a)** CO_2 (%) uptake as a function of rpm at 1 bar pressure **(b)** % CO_2 (%) uptake as a function of injection pressure at 300 rpm.

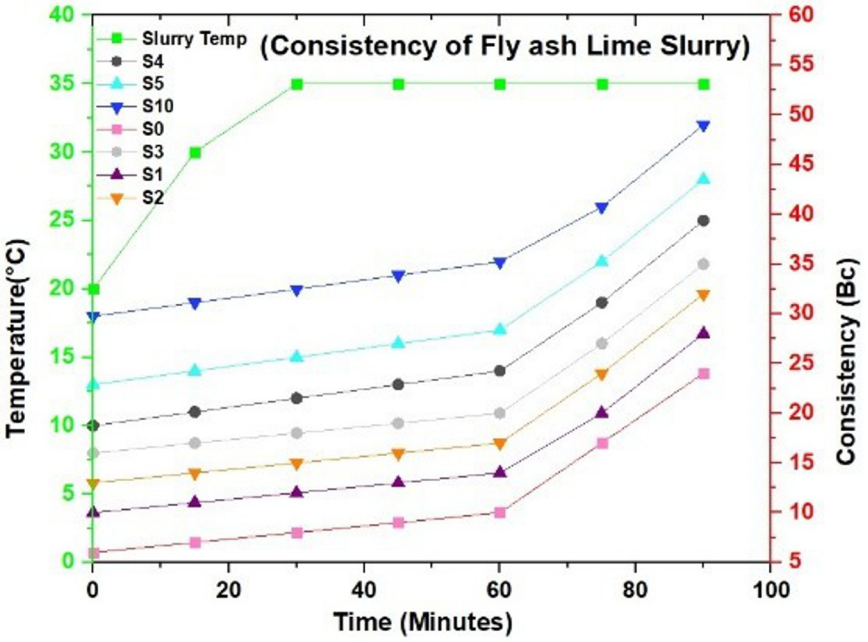

Fig. 6. Consistency studies of CFA-HL composites.

3.5 Consistency Test of Fly Ash Lime Slurry

The slurries were prepared according to the details in Table 1 and subjected to a consistency test performed as mentioned in section 2.2.7. All slurries were heated to 35 °C, and torque was measured over time. Slurries with higher water content exhibited a gradual thickening rate, as shown in Fig 6.

3.6 Free Water and Compressive Strength Assessment

Water is necessary for the hydration process of Fly ash lime composite block, where lime react with water to form a hardened matrix. If the free water content exceeds the amount required for hydration, it leads to the formation of voids as the excess water evaporates, reducing the block's strength. Fig 7(a) illustrates the free water content in various samples prepared according to Table 1. It was observed that the free water content decreased as the lime percentage increased from 0% to 4%, but no further reduction was noted with an increase to 5% and 10%. This could be attributed to the higher water content used during slurry preparation, which was 39% for the latter two samples, as indicated in Table 1. The compressive strength increased gradually with

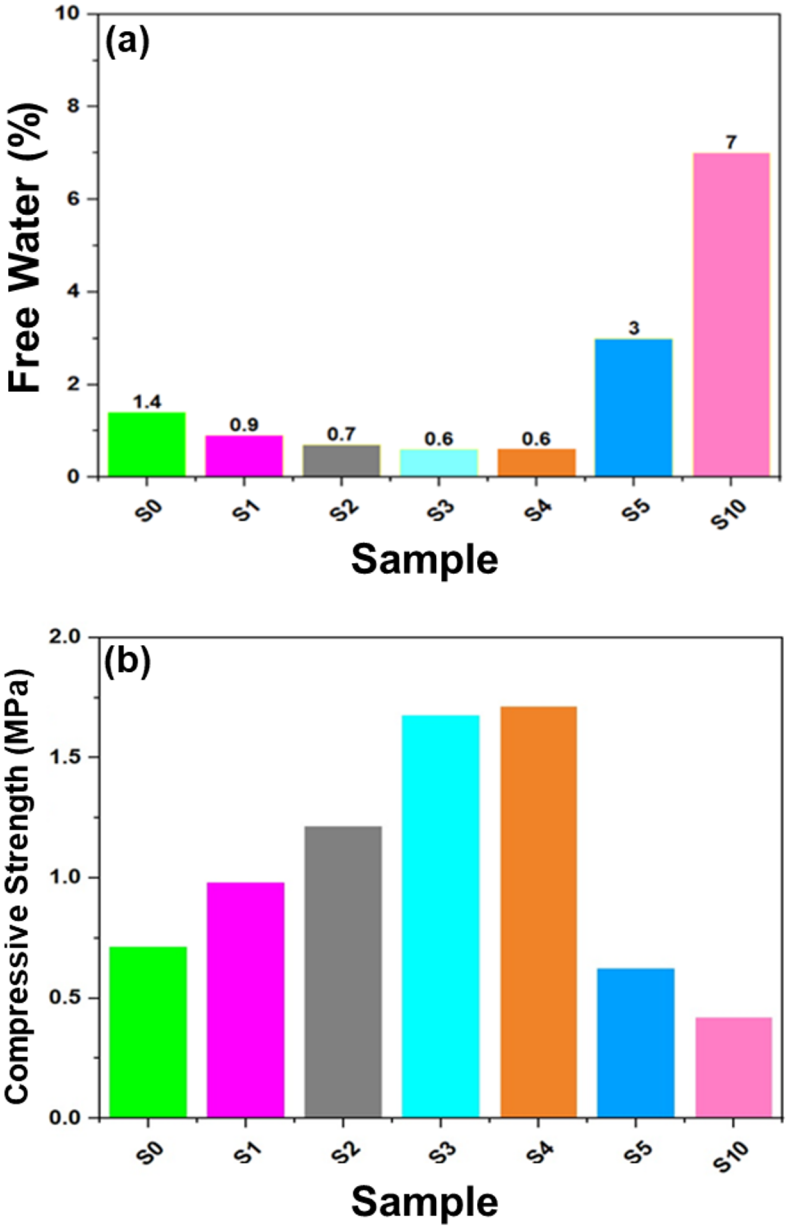

Fig. 7. Plots showing **(a)** Free water percentage **(b)** Compressive Strength of different samples.

increase in lime content up to 4% Fig 7(b). Thereafter, the compressive strength rapidly falls owing higher free water content.

4 Conclusion

This study highlights the effective utilization of Coal Fly Ash-F (CFA-F) from NTPC power station and hydrated lime (HL) for CO_2 sequestration through mineral carbonation, offering an eco-friendly solution to reduce CO_2 emissions while repurposing fly ash waste. The S4 composition, carbonated under specific pressures and agitation rates, achieved a peak compressive strength of approximately 1.7 MPa due to the synthesis of silicate hydrates and carbonates of calcium. Enhanced agitation and increased CO_2 injection pressure improved CO_2 sequestration (5.4%) and material strength, though no significant gains were observed beyond a pressure of 1.5 bar. This process provides a sustainable strategy for addressing CO_2 emissions and fly ash disposal challenges, offering a promising solution to environmental issues associated with thermal power plants.

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Disclosure of Interests. The authors declare that they have no competing interests relevant to the content of this article.

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