

CO₂ Sequestration Using Fly Ash from Lignite Power Plants [†]

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Abstract: Carbon dioxide sequestration by calcium- or magnesium-containing minerals has been recognized as a promising processing route for the permanent and safe storage of carbon dioxide. In this study, the wet carbonation of lignite fly ash containing approximately 39 wt.% of total calcium oxide was attempted in an autoclave at pressure 1–15 bar, temperature 25–150 °C, liquid to solid ratio equal to 10 L/kg and retention time 24 h. Carbon content in treated fly ash was increased due to carbonation from 1.76% to 4.84–6.15% with the maximum value obtained at temperature 100 °C and pressure 15 bar. The analytical techniques applied confirmed the elimination of free lime and the formation of CaCO₃. Based on the carbon content in untreated and treated samples it is estimated that under the optimum conditions 212,57 kg CO₂ are sequestered in 1 tn of fly ash.

Keywords: fly ash; lignite; carbon mineralization; carbon sequestration; CO₂



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1. Introduction

It is well known that carbon dioxide (CO₂) emitted to the environment mainly from fossil fuel combustion plants is considered one of the main contributors to the so-called “greenhouse effect”. According to the International Energy Agency (IEA), the CO₂ emissions from coal power plants rose to a record of 10.5 Gt, corresponding to 36% of total CO₂ emissions in 2021 with total energy-related CO₂ emissions rising to 36.3 Gt [1]. On the other hand, the EU aims to be carbon neutral by 2050, which is in line with the European Green Deal and the EU’s commitment to global climate action under the Paris Agreement.

Among the existing technological solutions, mineral carbonation, which has been proposed as an alternative approach since the 1990s [2], is a promising solution for economic CO₂ sequestration. It involves the reaction of feedstocks rich in calcium, magnesium, barium or iron to sequester carbon dioxide in the form of mineralogical phases remaining stable under long-term storage conditions [3].

Several sources of low-cost raw materials, by-products or waste have been investigated for mineral carbonation. Fly ash is a combustion by-product constituting about 60–88% of the total combustion residues from coal- and lignite-fired power plants. Worldwide, annual production is estimated at 0.75–1 billion tones and only a small percentage is utilized [4]. The lignite fly ash usually contains oxides, such as calcium oxide, and silicates that could be potentially react with CO₂ to form stable carbonate phases. The aim of the present study is to investigate the effects of different parameters on wet CO₂ sequestration by lignite fly ash with increased calcium oxide content.

2. Materials and Methods

The lignite fly ash sample was provided by the Greek Public Power Corporation collected from the Ptolemais power plant (Western Macedonia, Greece). Grain size distribution

was determined by laser particle analysis (Malvern microplus laser particle size analyser, Malvern Panalytical, Malvern, UK). Chemical analysis was performed by acid digestion followed by analysis of the solution by AAS (PinAAcle 900T, PerkinElmer, Waltham, MA, USA) and XRF (SPECTRO-XEPOS, SPECTRO Analytical, Kleve Germany). C and S were determined by LECO furnace analyzer (CS-200, LECO, St. Joseph, MI, USA). The free CaO was also determined by applying the ISO EN 451-1 method. Mineralogical analysis was performed by X-ray diffraction analysis (Bruker D8 Focus, BRUKER, Billerica, MA, USA), and scanning electron microscopy (Jeol6380LV, JEOL, Akishima, Japan) coupled with energy dispersive X-ray spectroscopy (EDS). Infrared spectroscopy analysis (Spectrum 100 Optical FTIR Spectrometer, SPECTRUM, Stamford, CT, USA) was applied to confirm phase formation. Thermogravimetric analysis was also conducted to determine the quantity of carbonates in the raw material before and after carbonation.

Carbonation experiments have been conducted in a 0.5 L autoclave (PARR 4841). In total, 10 g of fly ash was mixed with deionized water at a liquid to solid (L/S) ratio 10 l/kg, the slurry was agitated at 400 rpm and contacted with CO₂ for 24 h at a pressure between 1 and 15 bars, and a temperature of 25, 50, 100, 150 or 200 °C. Then, the suspension was removed, the pH was measured and the slurry was filtered using a 45 µm filter. The resulting solid residues were subjected to detailed chemical and mineralogical analysis including determination of acid neutralization capacity by titration with hydrochloric acid solution.

3. Results and Discussion

3.1. Fly Ash Characterisation

Fly ash is a very fine material, with 80% of the grains being finer than 63 µm. According to ASTM D433, the sand, silt and clay fractions are 12, 80 and 8%, respectively. The results of chemical analysis are given in Table 1.

Table 1. Chemical analysis of the representative fly ash sample.

Major Constituents (%)		Trace Elements (%)	
SiO ₂	25.14	Mo	0.16
Fe ₂ O ₃	5.28	Mn	0.04
Al ₂ O ₃	11.04	Cr	0.06
CaO	38.77	Cu	0.02
MgO	3.47	Ni	0.04
Na ₂ O	0.24	Co	0.04
K ₂ O	1.27	Zn	0.03
P ₂ O ₅	0.34		
TiO ₂	0.64		
C	1.73		
S	2.54		

As seen in Table 1, fly ash mainly consists of Ca, Si, Al, Fe, Mg, S and C. The free CaO was found to be 14.58 wt. %. Based on the chemical composition, the fly ash can be characterized as type C due to the high lime content (CaO/SiO₂ > 1).

X-ray diffraction analysis indicated that the main crystalline phases are: lime (CaO), mullite (Al₆Si₂O₁₃), quartz (SiO₂), gehlenite (Ca₂Al₂SiO₇), albite (NaAlSi₃O₈), hematite (Fe₂O₃) and periclase (MgO) (Figure 1). IR spectroscopy analysis also confirmed the presence of lime (CaO), hematite (Fe₂O₃) and quartz (SiO₂). Peaks corresponding to alumina (Al₂O₃), calcite (CaCO₃) and anhydrite (CaSO₄) were additionally identified.

3.2. Fly Ash Carbonation

The results with regard to the carbon content in carbonated fly ash as compared with untreated fly ash are given in Figure 2. As can be seen in this figure, the carbon content in treated fly ash was increased from 1.76% in the untreated fly ash sample to 4.84–6.15% in the treated samples depending on the experimental conditions applied, with an average value of 5.53 ± 0.34%. Statistically, there is a very small increase in carbon content when

the pressure increases from 1 to 15 bar. However, as the temperature increases up to 100 °C, the carbon content also increases (Figure 2) and then it decreases due to vapour production resulting in the decrease in the partial pressure of carbon dioxide introduced. The maximum carbon content (6.15%) was reached at a temperature of 100 °C and a pressure of 15 bar. In this experiment, the carbon content was increased by 27% compared with the experiment that resulted in a lower carbon content. Based on the values of carbon content in the untreated and treated samples under the optimal conditions, it is estimated that, overall, 212.57 kg of CO₂ is sequestered in 1 tn of fly ash. This value is higher than the amount of potentially sequestered CO₂ as determined based on free CaO and MgO content in fly ash, indicating that under the conditions applied other Ca-bearing minerals existing in fly ash are dissolved.

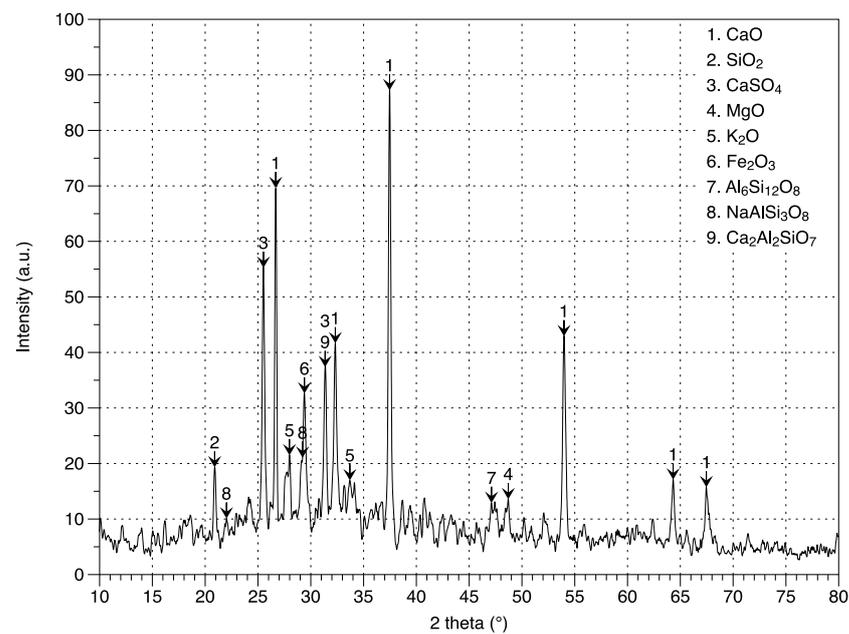


Figure 1. X-ray diffraction pattern of fly ash.

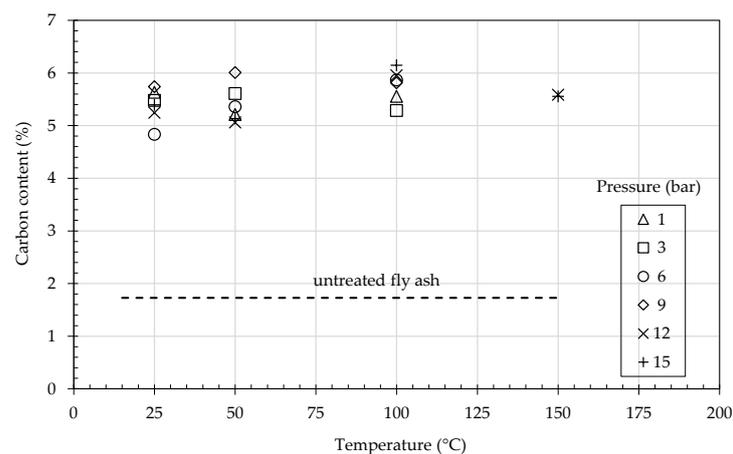


Figure 2. Total carbon content in fly ash vs. temperature and total pressure.

XRD analysis of the treated samples (Figure 3) indicated the elimination of CaO peaks (straight lines) and the appearance of new higher intensity peaks (dashed lines) of calcite formed during the reaction of carbon dioxide and calcium oxide. The peaks of MgO also disappeared, whereas several other transformations, e.g., the conversion of CaSO₄ to its hemihydrate form, the formation of tetracalcium aluminate hydrate (Ca₄Al₆O₁₃·3H₂O),

calcium silicates, etc. took place. Furthermore, SEM/microprobe analysis confirmed the presence of CaCO_3 in the treated fly ash samples, as given in Figure 4.

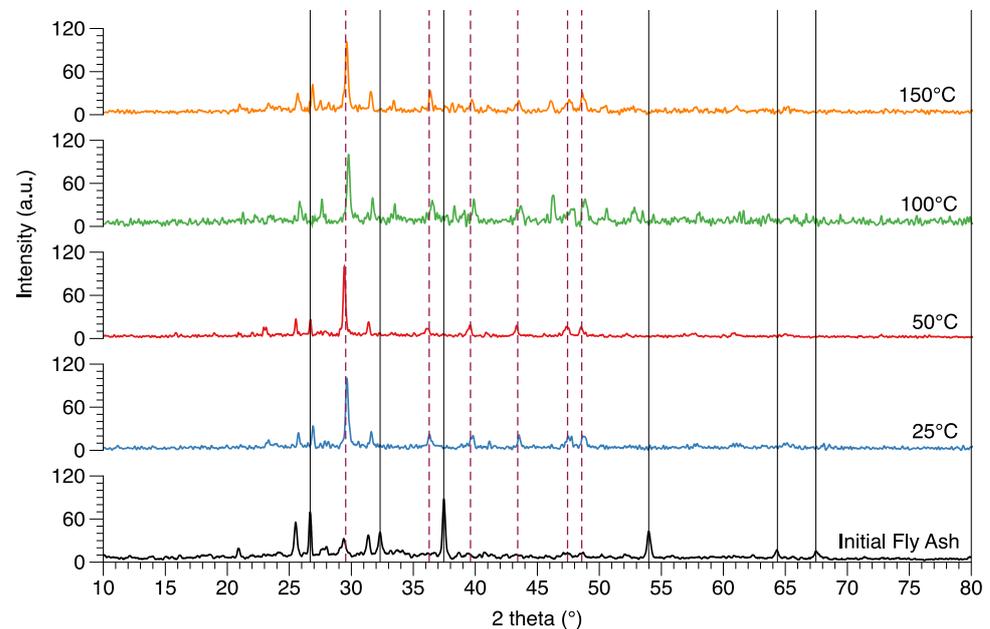


Figure 3. XRD patterns of fly ash carbonation products.

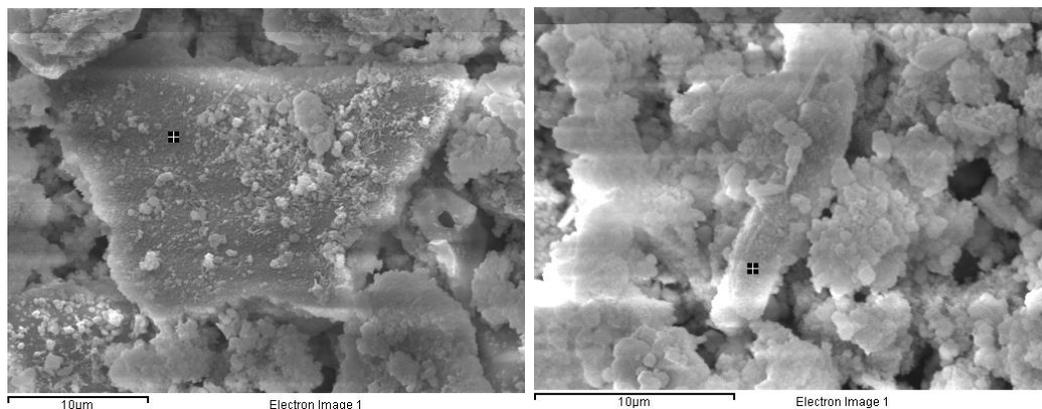


Figure 4. SEM images of calcium carbonate in treated fly ash samples.

The acid-neutralizing curve of non-treated sample is characterized by three (3) plateau areas at the approximate pH: 12, 10 and 8. The areas at $\text{pH} \approx 12$ and 10 correspond to the dissolution of CaO and the hydration of CaO to the formation of Ca(OH)_2 , respectively. Based on the acid-neutralizing curves, for the consumption of free Ca and Mg oxides 6.5 meq HCl per g of fly ash is needed. This value is close to the theoretical value of 6.9 meq/g fly ash determined based on the basis of the free lime and magnesium oxide content in fly ash. The acid-neutralizing curves of the treated fly ash samples do not exhibit the plateau areas at $\text{pH} \approx 12$ and 10, confirming the absence of free CaO and/or Ca(OH)_2 phases due to their participation in carbonation reactions.

4. Conclusions

Type “C” lignite fly ash with high free lime content has been proven effective for carbon dioxide sequestration. Carbonation experiments performed in an autoclave under various temperatures (25–150 °C) and pressures (1–15 bar) at L/S = 10 L/kg for 24 h indicated that the carbon content in treated fly ash was increased during carbonation from 1.76 % to 4.84–6.15% depending on the experimental conditions applied, with the

maximum carbon content obtained at temperature 100 °C and pressure 15 bar. Although the results are scattered, it is apparent that there is a very small increase in the carbon content when pressure increases from 1 to 15 bar and temperature increases up to 100 °C. XRD analysis, microscopic observation and acid-neutralizing capacity measurements indicated the elimination of free or hydrated lime and the formation of CaCO₃ grains due to CO₂ sequestration. Based on the carbon content values in untreated and treated samples, it is estimated that under the optimum conditions, in total, 212,57 kg CO₂ is sequestered in 1 tn of fly ash.

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