



## Technical Note

CO<sub>2</sub> carbonation under aqueous conditions using petroleum coke combustion fly ashA. González<sup>a,b</sup>, N. Moreno<sup>c</sup>, R. Navia<sup>b,d,\*</sup><sup>a</sup> Núcleo de Investigación en Energías Renovables, Universidad Católica de Temuco, Rudecindo Ortega 02950, Temuco, Chile<sup>b</sup> Scientific & Technological Bioresources Nucleus, University of La Frontera, P.O. Box 54-D, Temuco, Chile<sup>c</sup> Department of Geosciences, IDAEA-CSIC, C/Jordi Girona, 18-26, E-08034 Barcelona, Spain<sup>d</sup> Department of Chemical Engineering, University of La Frontera, P.O. Box 54-D, Temuco, Chile

## HIGHLIGHTS

- We use petroleum coke combustion fly ashes to capture CO<sub>2</sub>.
- We develop and use an accelerated aqueous CO<sub>2</sub> carbonation process.
- We measure CO<sub>2</sub> carbonation efficiency and kinetics in petroleum coke fly ash.

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## ABSTRACT

Fly ash from petroleum coke combustion was evaluated for CO<sub>2</sub> capture in aqueous medium. Moreover the carbonation efficiency based on different methodologies and the kinetic parameters of the process were determined. The results show that petroleum coke fly ash achieved a CO<sub>2</sub> capture yield of 21% at the experimental conditions of 12 g L<sup>-1</sup>, 363 °K without stirring. The carbonation efficiency by petroleum coke fly ash based on reactive calcium species was within carbonation efficiencies reported by several authors. In addition, carbonation by petroleum coke fly ash follows a pseudo-second order kinetic model.

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## 1. Introduction

Anthropogenic CO<sub>2</sub> results from fuels burning in power facilities and significant increase in CO<sub>2</sub> emissions is expected in the future due to the dependence on fossil fuels (IPCC, 2007). The Earth System Research Laboratory (2013) confirms a current atmospheric CO<sub>2</sub> concentration of 395 ppm, which is higher than the safety limit for atmospheric CO<sub>2</sub> (350 ppm). Scientists are concerned because the high atmospheric CO<sub>2</sub> concentration causes an increase in average global temperature. Some of the efforts to drastically reduce CO<sub>2</sub> emissions are reflected in the Kyoto Protocol with the current Doha Amendment.

Power facilities can achieve the CO<sub>2</sub> emissions reduction targets by means of CO<sub>2</sub> capture and sequestration (CCS) after combustion

(Kaithwas et al., 2012). CO<sub>2</sub> capture technologies using Ca–Mg bearing minerals are based on a chemical reaction (carbonation), which produces mineral carbonates with improved stability (Rendek et al., 2006). Accelerated mineral carbonation (MC) seems to be more effective and viable for industrial purposes, since operating variables are controlled to promote faster carbonation (Liu et al., 2001; Baciocchi et al., 2009). Nevertheless, MC presents disadvantages associated with high energy consumption in the grinding process and extraction of natural resources (Li et al., 2013). As humanity demands more renewable and natural resources than Earth can provide, it is necessary to find low cost, recyclable materials such as fly ashes (FA) to replace natural resources such as Ca–Mg bearing minerals. Research done in recent years has shown that FA recycling in MC process is an interesting approach due to on-site CO<sub>2</sub> capture (Wee, 2013).

FA are generated in large volumes and present a varied chemical composition depending on the combustion process (Blisset and Rowson, 2012). FA from lignite (Back et al., 2008; Bauer et al.,

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2011), coal (Mayoral et al., 2013), biomass (Gunning et al., 2010), and oil shale combustion (Uibu et al., 2009) have already been reported as potential alkaline materials for CCS. All authors stated that CCS by FA occurs by different carbonation pathways using a wide range of experimental conditions (Wee, 2013). In particular, it is observed that solid/liquid ratios used in MC process depend on their mineralogy, pore and particle size and also chemical composition (Hutzinger et al., 2009).

FA from petroleum coke combustion (PCFA) presents a high Ca content. It has been already suggested that PCFA is a suitable material for neutralizing acidic wastewaters and removing heavy metals (González et al., 2011). To date, PCFA has not been tested in CO<sub>2</sub> carbonation; this work therefore studies MC in aqueous conditions using PCFA, evaluating the effects of temperature, solid/liquid ratio and time on the percentage of CO<sub>2</sub> capture.

## 2. Materials and methods

### 2.1. Materials

PCFA from circulated fluidized bed combustion was selected for this study. PCFA sample was taken from the filter bags of a power plant located in Bio-Bio Region, Chile. González et al. (2011) detected as main elements in PCFA, Ca (34.1%), Mg (2.5%), Na (0.1%). Moreover, main Ca crystalline minerals are lime, portlandite and anhydrite.

Analytical grade reagents such as sucrose and water for chromatography (LiChrosolv) were obtained from Merck; CO<sub>2</sub> was provided by Linde Gas S.A with 99.9% purity.

### 2.2. Methods

#### 2.2.1. Carbon dioxide capture in aqueous medium

CO<sub>2</sub> capture is based on direct MC in aqueous medium. For this purpose, PCFA samples were blended with deionized water at different S/L ratios (6–50 g L<sup>-1</sup>). Slurries were placed in contact with pure CO<sub>2</sub> at a flow rate of 0.8 L min<sup>-1</sup> and at different reaction times (10–90 min) and temperatures (303–393 °K). After carbonation reaction, the slurries were filtered using a filter paper of 0.2 μm. The liquid was discarded and the carbonated PCFA was dried and stored for subsequent analysis.

The percentage of CO<sub>2</sub> capture in each sample was calculated by determining the inorganic carbon content (% C<sub>i</sub>) using a total organic carbon analyzer (TOC-V<sub>CPH</sub> Shimadzu) coupled with solid sample module SSM-5000A. The measurement of % C<sub>i</sub> consisted of the chemical reaction between the sample and phosphoric acid at 473 °K in the SSM-5000A, releasing CO<sub>2</sub> which is detected by an infrared detector. The measured % C<sub>i</sub> can be expressed as the CO<sub>2</sub> percentage (% CO<sub>2</sub>) according to Eq. (1):

$$\% \text{CO}_2 = \% \text{C}_i \frac{MW(\text{CO}_2)}{MW(\text{C}_i)} \quad (1)$$

where: MW is molecular weight (g mol<sup>-1</sup>)

#### 2.2.2. Carbon dioxide capture kinetics

The best data achieved by direct MC in the aqueous medium were used for the batch kinetic study. The procedure of CO<sub>2</sub> capture kinetics was performed according to Section 2.2.1. After carbonation, experimental data were fitted to a pseudo-second order model to predict CO<sub>2</sub> capture rate constants by PCFA (Ho and McKay, 1999).

#### 2.2.3. Estimation of theoretical CO<sub>2</sub> capture

For this purpose, two methodologies were used. In general, the theoretical CO<sub>2</sub> capture (Th-% CO<sub>2</sub>) is estimated using the Steinour

formula (Gunning et al., 2010), which is based on major elements content.

The second option is to use the modified ASTM C-25 (SCAN, 1981) procedure. In this procedure, lime and portlandite (reactive calcium species) content expressed as a percentage (% RCaS) is determined by means of a titration method under specific conditions.

Carbonation efficiency (CE) was also calculated. In this study, CE was estimated by Eq. (2) which compares the best CO<sub>2</sub> capture yield values obtained during carbonation experiments with the (Th-% CO<sub>2</sub>) yield, obtained from Steinour equation and the modified ASTM C-25 (% RCaS).

$$\text{CE} = \frac{\% \text{CO}_2}{\text{Th-\% CO}_2} \cdot 100 \quad (2)$$

## 3. Results and discussion

### 3.1. Carbon dioxide capture in aqueous medium

A significant indicator for CO<sub>2</sub> capture was the pH value. Prior to carbonation experiments, the PCFA exhibited a pH value in water of 12.5, caused by portlandite and lime dissolution. High pH value leads to fast dissolution of CO<sub>2</sub> in the aqueous medium. Afterwards, a chemical reaction occurs between calcium and carbonate ions. End pH values in the slurries after different reaction times decreased from 12.5 to 7.0. The strongest pH decline occurred between 60 and 90 min (Fig. 1a), which is due to neutralization process. It was also observed that low CO<sub>2</sub> capture values (around 13%) corresponded to high pH values (11.2–12.1), whereas high CO<sub>2</sub> capture values (19–20%) correlated to low pH values (7.0–9.1). Therefore, the pH value may potentially indicate the extent of carbonation by PCFA.

Results from the aqueous carbonation route indicate that PCFA is able to capture significant amounts of CO<sub>2</sub>. The experiments showed that the MC process by PCFA is very rapid (Fig. 1). All assays indicate that around a 10% of CO<sub>2</sub> is captured in the first 10 min (Fig. 1b), representing about 50% of the total CO<sub>2</sub> captured by PCFA at 90 min. It was further observed that higher CO<sub>2</sub> capture yields were reached with increasing reaction time.

Temperature plays an important role in carbonation by PCFA. As shown in Fig. 1b and c, higher CO<sub>2</sub> capture yields were obtained with increasing temperature. Reaction temperature has a strong implication for diffusion and dissolution, carbonation kinetics and thermodynamic constants (Hutzinger et al., 2009). Moreover, an increase in temperature can provoke two opposite effects. One of these is related to Ca-dissolution, which is favored by increasing temperature; the other effect is the solvation and hydration of CO<sub>2</sub> which is limited by increasing temperature. Experimental results at 10 and 90 min indicate an increase in CO<sub>2</sub> capture with increasing temperature up to 363 °K (Fig. 1b and c). The best CO<sub>2</sub> capture values were achieved by using 333 and 363 °K (Fig. 1c). The results are in accordance with temperature range between 294 and 453 °K reported by Liu et al. (2001).

Turning to S/L ratio, several authors state that carbonation depends strongly on the presence of water with the optimum S/L ratio reported as being between 5 and 17 g L<sup>-1</sup> (Li et al., 2013). For these experimental tests, the higher CO<sub>2</sub> capture yields were obtained for an S/L range between 12 and 25 g L<sup>-1</sup>, and it is observed that as the volume of water decreases, larger CO<sub>2</sub> capture yields are obtained. Nevertheless, in this study, this observation is only corroborated for temperatures lower than 393 °K. This could be attributed to minor blocking of the solid pores of PCFA, a high CO<sub>2</sub>/H<sub>2</sub>O interface area and short diffusion routes to the PCFA surface, leading to higher CO<sub>2</sub> availability, higher CO<sub>2</sub> capture yields

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