Applied Energy 142 (2015) 274–282

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Leaching and indirect mineral carbonation performance of coal fly ash-water solution system

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HIGHLIGHTS

- Wet indirect mineral carbonation is conducted using fly ash (FA) as source materials.
- Overall CO_2 storage capacity of FA suspended solution is 31.1 mg CO_2/g FA.
- Maximum mineral carbonation capacity of FA suspended in solution is 17.4 mg CO_2/g FA.
- Alkaline components are leached from suspended FA during mineral carbonation.
- Tiny particles in FA strongly affect the mineral carbonation performance.

ARTICLE INFO

Article history:
Received 23 July 2014
Received in revised form 24 December 2014
Accepted 26 December 2014
Available online 17 January 2015

Keywords:
Mineral carbonation
Leaching
Coal fly ash
Carbon dioxide capture and storage
Coal fired power plant

ABSTRACT

The leaching and carbonation performances of indirect mineral carbonation are investigated using coal fly ash (FA) as the raw source and water as the solvent. The reactions were conducted at ambient temperature and pressure with a gas mixture comprised of 15 and 33 mol% CO_2. The overall CO_2 storage and mineral carbonation capacities of FA suspended solution in which alkaline components had been previously leached for 2 h (2S33) were 31.06 and 17.36 mg CO_2/g FA, respectively. The mineral carbonation capacity of FA in 2S33 was 18% of the theoretical value and its mineral carbonation storage capacity ratio was 55.9%. The performance of 2S33 was higher than that of its filtrate because the alkaline components were leached from the suspended FA simultaneously with the mineral carbonation. Submicrometer-sized particles were present in raw FA and their size was reduced by stirring during the leaching, as well as slightly increased, compared to the original raw FA, due to the carbonation. These submicro FA particles strongly affected the performance of the mineral carbonation of the FA-water solution.

1. Introduction

Mineral carbonation is a technology for permanently fixing CO_2 by producing stable carbonate materials via the reaction of CO_2 with alkaline components present in mineral and industrial residue, such as Ca, Mg, Na, and K [1,2]. This technology has recently received much attention because of its many advantages, particularly its small environmental load in terms of product disposal [3–5].

Mineral carbonation can be classified into direct and indirect processes [6,7]. In the former, the raw source materials containing the alkaline components are directly injected into the carbonation process for the reaction of CO_2 and alkaline components. In the latter, the alkaline components are extracted from the source materials by leaching, after which the carbonate materials are generated by carbonation. In addition, mineral carbonation can be divided into dry (gas–solid) and wet (gas–liquid or gas–liquid–solid (slurry)) processes according to the phase in which the carbonation occurs [2,8]. Although the dry process is relatively simple in terms of reaction route and the heat generated by the carbonation reaction is easily applied because CO_2 is reacted with the alkaline components in the solid phase, its slow reaction rate and low carbonation ratio are the major limitations [2,8,9]. Whereas, the reaction rate of the wet process is fast because the alkaline components are present as reactive ions in the aqueous solution [10]. In addition, the input and output of the liquid absorbent can be effectively controlled in the process. However, the recovery of heat from the carbonation and its management are more difficult than in the dry process.

Alkaline components are present in coal fly ash (FA) generated from the combustion and desulfurization (FGD) process of

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http://dx.doi.org/10.1016/j.apenergy.2014.12.074
0306-2619/

coal-fired power plants (CFPP). Therefore, FA has great potential to be used as a raw source material for the mineral carbonation to reduce CO_2 emissions [2,9,11–13]. However, most FA is currently used as a cement additive to increase the concrete strength [14–16]. The development of a suitable mineral carbonation technology using FA for CO_2 emission reduction will help maximize the economic, technological and environmental benefits of FA application to on-site CFPP [7,9,13].

Although many studies focusing on FA application to mineral carbonation have been conducted [3,17–19], the wet indirect process has been preferred due to the characteristics of FA such as the presence of extractable alkaline components under acidic solution condition [20,21]. Therefore, more extensive information on the leaching and carbonation performance of FA is essential for developing the technology as well as FA disposal. In the literature, many studies have investigated the leaching efficiency using acidic solvents such as brine, saline, waste acid and acidic rain [22–24], and have measured the carbonation capacity under highly pressurized condition with already captured CO_2 to increase the carbonation capacity. However, a large amount of energy is consumed to maintain the high pressure during the carbonation [25–27]. In some works, neutral or alkaline aqueous solution was used as the solvent for leaching and the carbonation was carried out at ambient temperature and pressure. However, the resulting performance was relatively poor and the results were not explained in terms of the relevant theoretical background to the leaching process [6,28].

In the present paper, wet indirect mineral carbonation was conducted using FA as the raw material source. The overall leaching characteristics were evaluated and the carbonation performance was investigated in detail. Water was used as the solvent and the reactions were carried out at ambient temperature and pressure in order to minimize the energy consumption. CO_2 composition in the gas mixture for carbonation was set at 15 and 33 mol%. Finally, the precipitates produced from the mineral carbonation were analyzed to probe the reaction mechanism.

2. Theory

The overall CO_2 storage capacity of FA, including the solution used as the leaching solvent and as the carbonation absorbent, is calculated according to Eq. (1).

$$\text{Overall } CO_2 \text{ storage capacity}(\text{g } CO_2/\text{g fly ash}) = \frac{m_{\text{abs}} - m_{\text{physics}}}{m_{\text{FA}}} \tag{1}$$

Here, m_{abs} is the total amount of CO_2 absorbed in the system, which is calculated by the variation of CO_2 concentration measured by a gas analyzer during the carbonation. m_{physics} is the amount of CO_2 physically absorbed into distilled water (DW) at ambient temperature and is assumed to be 0.19 and 0.52 g CO_2/0.5 L of DW at a CO_2 composition of 15 and 33 vol%, respectively [29]. m_{FA} is the amount of FA used as the raw material for mineral carbonation.

The FA was generated in Yeong-heung CFPP (South Korea) and its composition is listed in Table 1.

Alkaline earth (M_{AE}^{2+}) and alkaline (M_A^+) metal ions leached from FA by DW can fix CO_2 according to Eqs. (2)–(5).

$$M_{AE}^{2+} + CO_3^{2-} \rightarrow M_{AE}CO_3 \tag{2}$$

$$M_{AE}CO_3 + CO_2 + H_2O \rightarrow M_{AE}(HCO_3)_2 \tag{3}$$

$$M_A^+ + CO_3^{2-} \rightarrow M_{A_2}CO_3 \tag{4}$$

$$M_{A_2}CO_3 + CO_2 + H_2O \rightarrow 2M_AHCO_3 \tag{5}$$

M_{AE}^{2+} can capture and store a constant amount of CO_2 in the form of carbonate materials ($M_{AE}CO_3$) by Eq. (2) and it can additionally absorb CO_2 in the form of $M_{AE}(HCO_3)_2$ according to Eq. (3). However, Eq. (3) is a very limited reaction due to its very low equilibrium constant. In addition, although CO_2 can be also stored by Mg via Eqs. (2) and (3), the amount of CO_2 fixed by Mg is negligible due to the very low leaching efficiency of Mg [30,31]. Meanwhile, M_A^+ captures CO_2 via Eq. (4) to be $(M_A)_2CO_3$, which is co-precipitated with $M_{AE}CO_3$ and present in the form of HCO_3^- absorbing additional CO_2 via Eq. (5) in the carbonation.

Table 1
Elemental composition in raw coal fly ash (FA): loss of ignition; 4.1%.

Element	Concentration (mg/g FA)	Element	Concentration(mg/g FA)
Ca	42.28	P	1.29
Mg	11.88	Na	19.82
Al	134.14	K	9.36
Fe	33.52	O*	586.45
Cr	0.04	C*	44.12
Ti	7.82	Si*	159.99

* Calculated based on EDX results.

The pH control during the carbonation process is very important because the precipitated $CaCO_3$ dissolves at pH lower 8.3 [6]. In order to investigate the amount of CO_2 fixed by the precipitation of carbonate materials excluding Eq. (3), the amount of CO_2 absorbed at pH higher 8.3 was calculated and termed the 'Mineral carbonation capacity'. All of the CO_2 absorbed at pH higher 8.3 is assumed to be consumed by mineral carbonation, and not physical absorption, because the chemical reaction of mineral carbonation is more dominant than physical absorption in this pH range [29]. Finally, the mineral carbonation ratio is calculated according to Eq. (6).

$$\text{Mineral carbonation storage capacity ratio} = \frac{\text{Mineral carbonation capacity}(\text{g } CO_2/\text{g FA})}{\text{Overall } \; CO_2\text{storage capacity}(\text{g } CO_2/\text{g FA})} \tag{6}$$

Meanwhile, the CO_2 absorbed at pH under 8.3 reduces the pH of the solution, which increases the leaching of the alkaline component from FA and participates in Eqs. (3) and (5).

3. Experimental

3.1. Preparation and leaching of coal fly ash (FA)-water solution for mineral carbonation

For the mineral carbonation, three kinds of solution were prepared as absorbent by mixing of DW and FA generated from CFPP without any pre-treatment such as sizing and elimination of unburnt carbon. The solid–liquid ratio of all absorbents was 50 g FA/L DW and the solutions were classified into 'leachate' and 'suspension' depending on whether the solution was filtered after leaching. For convenience, all solutions were abbreviated as "L" and "S" for leachate and suspension, respectively. In addition, the leaching time of suspension in units of hours was designated in front of this solution abbreviation. For example, '2S' means FA suspended solution not filtered after leaching for 2 h.

Leaching of FA suspended solution was conducted in a Pyrex reactor (D; 110 mm, h; 80 mm, total volume is about 500 mL above) with a water jacket where the temperature was maintained at 25 °C. A lab stirrer (PL-S20, Poonglim) was used to maintain the stirring speed of 300 rpm. When filtration was required to obtain the filtrate, filter paper with pore size of 0.1 μm was used.

3.2. Mineral carbonation

Carbonation was carried out with 500 mL of the solution and a schematic diagram of the reaction is shown in Fig. 1.