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Research article

CO_2 sequestration by direct mineralisation using fly ash from Chinese Shenfu coal

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ABSTRACT

Fly ash is a potential source of highly reactive feedstock for CO_2 mineral carbonation. It does not require pre-treatment, but it has a low carbonation rate and efficiency. To address these issues, we studied the carbonation performance and mechanism of a fly ash from Shenfu coal of China. The effects of temperature, solid to liquid ratio and gas flow rate on the carbonation efficiency of the fly ash were systematically investigated in a direct mineralisation process. Our results indicated that calcium in lime and portlandite had a higher reactivity towards CO_2 than that in other calcium bearing phases either crystalline or amorphous. Solely increasing the temperature did not improve carbonation efficiency. However, experiments in a batch reactor under elevated temperature (140, 180, and 220 °C) and pressure conditions (10 and 20 bar) using recyclable additives showed that a combination of high temperature and pressure significantly improved carbonation efficiency in the presence of 0.5 mol/L Na_2CO_3. Our multiple-cycle experiments showed that Na_2CO_3 facilitated the precipitation of calcium carbonate and was well regenerated in the process.

1. Introduction

CO_2 sequestration by mineralisation is one of the safest and most permanent methods for storing CO_2 emitted by fossil fuel combustion, and could be a viable alternative to CO_2 geological storage [1,2]. It is suitable for small and medium emitters, or wherever geological storage is not possible [3–6]. Comparing to natural minerals, industrial by-products such as fly ash have several advantages to be the feedstock, including low materials cost, high materials reactivity, no pre-treatment requirement, and ease of availability near CO_2 emission sources [4–7]. Specifically, fly ash normally contains alkaline oxides such as CaO and MgO which are seen as the ideal feedstocks for CO_2 sequestration because of their high reactivity. Also, fly ash generally is fine enough with the majority of the particles falling in micron or even submicron scale, and grinding is not required prior to the carbonation process. In addition, fly ash is generated with CO_2 together after combustion in coal-fired power plants, so it does not need any extra cost of transport [8].

By 2015, >580 million tonnes of fly ash were estimated to be generated annually from coal-fired power plants in China, accounting for >50% of global production [9,10]. As a toxic by-product of coal combustion that is generated in such huge amounts, the disposal of fly ash has become a serious problem. Technologies have been developed to utilize this residue in construction materials production [9]. Fly ash normally contains active species, such as CaO and MgO, so that blended cement or concrete containing fly ash could gradually absorb moisture from the air and cause expansion in the product life cycle [11], which is one of important factors stopping fly ash from widespread application in construction industry. Using fly ash to sequester CO_2 can not only reduce the CO_2 emission but also increase fly ash stability thus expanding its utilization in construction material production. However most Chinese fly ashes have a lower CO_2 sequestration capacity [6,9] than other industrial wastes rich in CaO such as steel slag (calcium oxide content is normally 32–52%)[6] because of the low content of these CO_2 reactive species in most Chinese fly ashes (normally <15%) [9]. Despite the low capacity, using fly ash as feedstock for CO_2 mineral carbonation is still attracting wide attention because of the huge volumes of annual production.

Mineral carbonation processes can be divided into two routes: direct and indirect. The indirect route is initiated by dissolution of mineral species in an aqueous medium to extract the alkaline-earth metals. The leachate, rich in alkaline-earth metal cations, is subsequently carbonated by CO_2, or by other carbonates (e.g. $NaHCO_3$/Na_2CO_3) obtained from

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other capture systems [7]. Recent studies of indirect route have focused on investigate different leaching agents [4,5,8]. Indirect route can produce more valuable pure carbonates than direct route, because impurities such as silica and iron can be removed prior to carbonate precipitation. However, the difficulty in recycling the leaching agents and the low alkaline-earth metals extraction ratio is hindering the application of this technology on a large scale [12,13]. In addition, calcium and magnesium are already present as carbonates in some fly ashes. Leaching agents could react with these carbonates and release CO_2 before they are re-carbonated [4].

Research on mineral carbonation of CO_2 using coal fly ash has focused mainly on direct aqueous route [14], which involves a direct reaction of fly ash with CO_2 in a single reactor, with water or brine as the reaction medium. The advantages of direct route are its simplicity and the minimal use of chemical reagents, which make it the most promising technology of CO_2 sequestration using fly ash [6,14]. Many recent studies have investigated effect of various parameters, such as temperature, CO_2 pressure, solid to liquid ratio, stirring rate, and reaction time, on the carbonation reaction of various fly ashes in aqueous system [15–24]. Carbonation efficiency and CO_2 sequestration capacity are widely used in these existing studies [15–26] to estimate the carbonation performance of various fly ashes. Some other studies have introduced additives to improve fly ash carbonation [25,26]. For example, Soong et al. [25] developed a process for carbonation of fly ash in brine solution in the presence of NaOH as an additive in an autoclave reactor and claimed that the CO_2 sequestration capacity of the mixture is higher than when using fly ash-water slurry and brine, respectively. Calcium from both the brine and fly ash contribute to the formation of calcium carbonate.

Despite the previous research, there is still knowledge gap on our understanding of the reaction mechanism involved in carbonation reaction. The effect of chemical properties of fly ash on carbonation efficiency is not fully understood either. Carbonation efficiency can be affected by not only the process parameters but also the heterogeneous chemical properties of fly ashes and the proportion of Ca/Mg-bearing mineral phases available for carbonation reaction. Actually, the mineral phases of different fly ashes represent various constitutions. The factors controlling this variation probably include the mineralogy and inorganic geochemistry of the raw coals, as well as the different combustion conditions [27–31]. For example, the principal crystalline phases present in fly ash from black coals are mullite, quartz, magnetite, maghemite, and hematite, while the main crystalline phases in lignite are quartz, lime, anorthite, mullite and anhydrite [27]. During the cooling stage after combustion, the lime can react with CO_2, H_2O and SO_2 from the flue gas, and was converted into $Ca(OH)_2$, $CaCO_3$, and $CaSO_4$ [28], or combined with amorphous phase. Thus, the mineral phases of various fly ashes involved in carbonation reaction can be very different. It is important to understand the effect of mineral phases on carbonation reaction because it can help improve our understanding of carbonation mechanism and develop more effective methods to promote carbonation reaction. Especially given the large volume of fly ash produced in China, it is important to understand more about the characteristics of Chinese fly ash in carbonation process, for which very limited published data is available.

In this study, the aim was to investigate the sequestration potential of a fly ash from Chinese Shenfu coal [32] in direct aqueous mineralisation process, to improve the understanding of the effect of various operating parameters on carbonation performance, to verify the mineral phase changes of fly ash before and after carbonation, and thus develop a method to further improve carbonation efficiency. We also investigated the role of additives such as Na_2CO_3, $NaHCO_3$ and NaCl in carbonation reaction using fly ash. The carbonation experiments were first carried out at moderate temperature and ambient pressure in a semi-batch reactor, in which CO_2 gas was bubbled through fly ash and water slurry. The changes in the mineral phases of the fly ash before and after carbonation were determined by quantitative XRD analysis to study the carbonation behaviour of different Ca-bearing mineral phases. Carbonation experiments were also conducted in a closed reactor under elevated conditions (higher temperature and pressure) and in the presence of additives including Na_2CO_3, $NaHCO_3$ and NaCl. We also performed a multiple-cycle carbonation process to investigate the regeneration and recycling of Na_2CO_3, the most effective additive investigated in this work.

2. Materials and methods

2.1. Materials

The fly ash used in this study was collected from the fifth stage of electrostatic precipitators of Huaneng Gaobeidian power plant in Beijing, which is based on Chinese black coal from Shenfu, Shanxi province. Na_2CO_3 (⩾99.5%), $NaHCO_3$ (⩾99.7%), and NaCl (⩾99%) chemicals were purchased from Sigma-Aldrich. All of the fly ash samples were dried overnight prior to any test. The elemental composition of the fresh samples was determined by X-ray fluorescence spectroscopy (XRF), while the crystalline phases present in fresh and carbonated samples were determined by XRD analyses. The XRD analyses were run on an Empyrean Panalytical X-Ray Diffractometer using CuKα radiation at 40 kV and 40 mA. Step scans were undertaken from 2 to 90° 2θ, with a step interval of 0.02° 2θ. The phase identification was performed using the Bruker Eva software package. The quantitative phase analysis was done using Siroquant™, which uses the Rietveld method to perform full profile matching [33–35]. The amount of amorphous matter in the ash was determined using an observed (hkl) file of an amorphous clay material, which was experimentally determined [33]. An inferred chemical composition for the amorphous fraction was calculated by subtracting the elements' percentage of crystalline phases from the bulk chemical composition [33,34]. The detailed description and validation of the method for calculation of chemical composition of amorphous phase in fly ash was published previously [33,34]. Total inorganic carbon (TIC) was determined by a Shimadzu TOC-L CPH C-analyser.

The calcium carbonate content of fresh and carbonated samples, expressed in terms of CO_2, was determined by a Netzsch STA 449 F1 Jupiter system coupled to a Pfeiffer Thermostar mass spectrometer. Mass changes as a function of temperature were measured by TGA, and evolved gases during thermal decomposition of materials were identified and monitored by the mass spectrometer. For each test, samples (10–20 mg) were heated in aluminium oxide ceramic cups under a nitrogen atmosphere at 10°/min from 30 to 950 °C. The temperature was held for 15 min at 105 °C and 600 °C, respectively, and then for 30 min at 950 °C. The mass spectrometer simultaneously analysed the evolved gases, including CO_2 and H_2O and confirmed that the weight loss at 30–105 °C, 105–600 °C and 600–950 °C was caused by evaporation of water, thermal decomposition of hydroxide, and thermal decomposition of carbonates, respectively [26,35–36] (Fig. 1). The amount of CO_2 in the fresh sample Eq. (1) was defined on the basis of its dry weight at 105 °C ($m_{105\ °C,\ 0}$, [g]) and its weight loss between 600 and 950 °C ($\Delta m_{600-950\ °C,\ 0}$, [g]) which is indicated in Fig. 1.

$$CO_{2,0}[wt\%] = \frac{\Delta m_{600-950\,°C,0}[g]}{m_{105\,°C,0}[g]} \times 100 \quad (1)$$

The weight loss of CO_2 in carbonated sample was from two parts: the decomposition of $CaCO_3$ contained in the fresh sample and the decomposition of $CaCO_3$ formed in the carbonation process. The CO_2 weight loss of the former part ($\Delta m'_{600-950\,°C}$, [g]) was calculated by Eq. (2):

$$\Delta m'_{600-950\,°C}[g] = \frac{m_{105\,°C}[g] - \Delta m_{600-950\,°C}[g]}{m_{105\,°C,0}[g] - \Delta m_{600-950\,°C,0}[g]} \times \Delta m_{600-950\,°C,0}[g] \quad (2)$$

where $m_{105\ °C}$ [g] is the dry weight of the carbonated sample at 105 °C, and $\Delta m_{600-950\ °C}$ [g] is the weight loss between 600 °C and 950 °C for the