

AN OVERVIEW OF ACCELERATED CARBONATION OF COAL COMBUSTION FLY ASH FOR ATMOSPHERIC CO₂ SEQUESTRATION AND SOIL AMENDMENT

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ABSTRACT

Fly ash is one of the most common solid by-products of coal combustion for electricity production. Currently, the majority of fly ash produced throughout the globe is discarded as trash with no practical use. Only a tiny percentage of overall fly ash output is utilized in cement manufacture, mineral wool manufacturing, metal recovery, road sub-base construction, mine reclamation, and agriculture. Furthermore, fly ash is a substance that may be utilized to collect and store CO₂ in the atmosphere via mineral carbonation, both in situ and ex situ of the source of CO₂. Accelerated carbonation has recently been investigated by scientists as a method of boosting the pace of mineral carbonation. In addition to attaining the advantages of carbon sequestration, rapid carbonation may render fly ash chemically stable, which can help overcome issues with hazardous element leaching when used as a soil supplement. As a result, this solid waste material may be effectively handled via rapid carbonation followed by addition to soil. The mineralization process's effectiveness is determined by the mineralogy, physical and chemical characteristics of fly ash, and reaction circumstances such as CO₂ partial pressure, temperature, relative humidity, and gas-to-material contact time. It is critical to choose material with the necessary characteristics and to provide it with the optimal reaction conditions in order to achieve greater CO₂ sequestration efficiency. The major problems surrounding the accelerated carbonation of coal combustion fly ash under various reaction circumstances and its impact on CO₂ sequestration efficiency are discussed in this article. It also highlights the possibility of using carbonated fly ash to enhance the physical and chemical characteristics of soil.

KEYWORDS: Carbonation, CO₂Sequestration, Coal Fly Ash, Metal Leachability, Soil Amendment.

1. INTRODUCTION

The other two main fossil fuel resources that are combusted for energy are oil and natural gas. Coal is one of the three primary fossil fuel resources in the world that are combusted for energy. Due to growing demand for power and the availability of coal deposits in many areas of the globe, coal combustion alone provides up to 40% of total global energy, and these numbers are steadily rising [1]. When coal is burned, two kinds of ashes are produced: fly ash and bottom ash,

which have approximate mass percentages of 90% and 10%, respectively. The electrostatic or mechanical precipitation of dust-like particles from the flue gas stream produces fly ash (FA). By the year 2000, the world's total coal FA output had reached approximately 600 million tonnes, with only 20% of it being beneficially used, mostly in the cement sector [2]. FA is a fast accumulating solid waste substance that poses significant disposal challenges until a large-scale solution can be discovered.

Simultaneously, the danger of global warming brought on by increased amounts of carbon dioxide (CO₂) in the atmosphere is prompting scientists to look at greenhouse gas mitigation methods [3]. As a result, a lot of research is being done on different methods of capturing and storing (sequestration) atmospheric CO₂. The injection of super-critical CO₂ into geological media such as deep seas, underground coal formations, salty aquifers, and depleted oil/gas reservoirs is a popular technique of CO₂ sequestration used all over the globe. Furthermore, the conversion of marginal land to forest results in the storage of atmospheric carbon in above-ground plant biomass and its contribution to the soil organic carbon pool. The use of alkaline materials for CO₂ sequestration through mineral carbonation has piqued the scientific community's attention as a novel idea. CO₂ reacts with minerals to produce solid carbonates in mineral carbonation [4]. Because the mineral carbonates are stable throughout geological time periods of millions of years, rather than the hundreds to thousands of years anticipated for other types of sequestration, this technique is really permanent. Carbonation of alkaline solid waste materials (e.g., coal fly ash/bottom ash, municipal solid waste incinerator fly ash/bottom ash, oil shale ash, steel slag, and cement kiln dust) for permanent CO₂ sequestration provides additional environmental benefits by assisting in the environmentally sound management of these solid wastes. Furthermore, if mineral carbonation is added as a last step to incinerator facilities, it opens up the potential of selling carbon credits for incineration businesses.

Apart from its uses in the cement and geopolymer sectors, coal combustion FA is gaining popularity as a material with the potential to improve soil characteristics [5]. Researchers have discovered that by using FA's self-cementing characteristics, it may be used to design soils and improve soil stability. FA has also been found to enhance agronomic characteristics of soil, including as moisture-holding capacity and hydraulic conductivity, soil structure and texture, pH buffering capacity, and macro- and micronutrient availability. FA, on the other hand, is not sold as a fertilizer or a soil ameliorant because of the risk of dangerous trace elements contaminating soil and ground water at large doses, as well as the unfavorable pH changes produced by the addition of certain FAs.

As a result, pre-treatments are often suggested before applying FA to soils in order to remove harmful materials and correct the pH. After the addition of FA to soil, weathering helps to decrease the leachability of hazardous elements, particularly boron (B), according to Pandey and Singh. Nonetheless, it has the potential to pollute groundwater at disposal sites. Because the carbonation reaction has been shown to change the chemical stability of ashes and enhance their leaching behavior, adding carbonated FA to soil may be a preferable choice. Furthermore, carbonation lowers the alkaline pH of the ashes to a level that is acceptable for use in soil. Mineral carbonation of FAs happens spontaneously in collecting ponds when they are exposed to ambient CO₂ and moisture [6]. This spontaneous carbonation process, which resembles rock weathering, does, however, require geological time to complete. As a result, achieving FA carbonation and ambient CO₂ removal rates equal to emission rates requires significantly slower

CO₂ absorption efficiency under natural carbonation. Accelerated carbonation with improved reaction conditions has the potential to cut carbonation time in half or even days. As a result, it seems to be a feasible method for capturing and storing atmospheric CO₂ in a stable state.

2. DISCUSSION

2.1. Properties of Coal Combustion FA:

FA refers to the amount of ash generated by coal combustion that is tiny enough to be transported away from the boiler in the flue gas. It's a heterogeneous material having a complicated amorphous (glassy) structure and perhaps some crystalline phases. Silica (SiO₂), alumina (Al₂O₃), and iron oxides are the main components of the FA matrix (Fe₂O₃). As significant mineral phases, it also includes minor amounts of quartz, mullite, hematite, and magnetite. FA has different mineralogical, physical, and chemical characteristics according on the kind of coal burnt, boiler type, collector set-up, and collector efficiency. As a result, the compositions of the ashes generated by the burning of bituminous, anthracite, and lignite coals vary. Depending on the quantities of calcium, silica, alumina, and iron in ash from the parental coal, two classes of FA may be identified: (a) Class F and (b) Class C. Class C FA is made from the combustion of lignite or sub-bituminous coal and often includes more than 20% lime (CaO) [7]. The pozzolonic activity of these ashes, which is mainly controlled by the CaO concentration, is a self-cementing action. When harder and older anthracite and bituminous coals are burned, Class F FA is produced, which contains less than 10% lime.

The texture of FA particles is extremely fine, with a grain size range ranging from sandy silt to silty loam. Particle diameters vary from 0.01 to 100 μm, although the majority of particles in a sample are 2–20 μm in diameter, which falls within the silt size range. FA is generally described as spherical non-opaque having a surface area of approximately 1 m²/g morphologically. Solid spheres, hollow spheres, irregularly shaped spheres, and spheres filled with smaller spheres are all possibilities. A scanning electron micrograph (SEM) of an FA sample, exhibiting its characteristic spherical shape and size range, is shown in Figure 1.

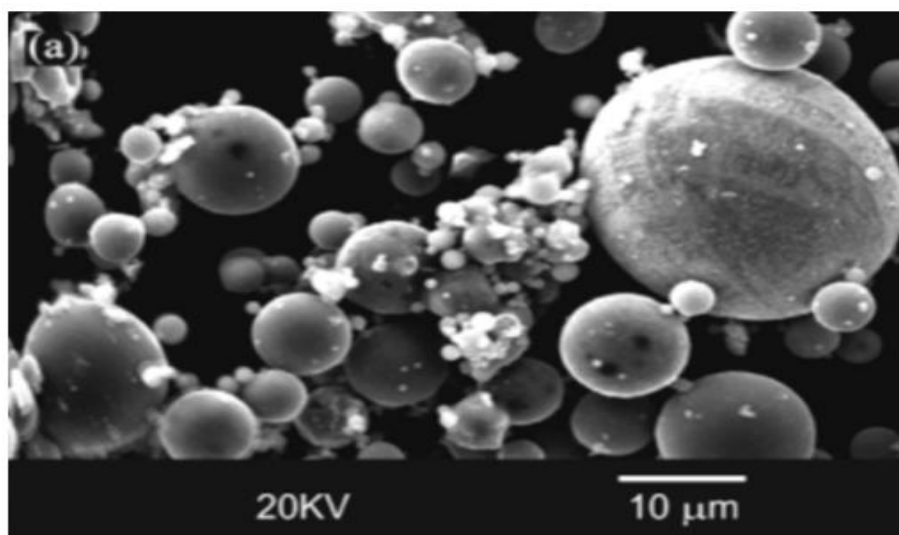
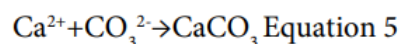
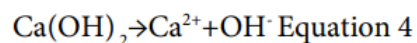
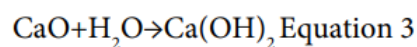
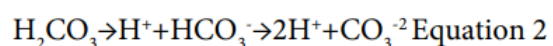
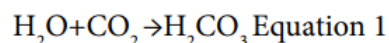


Figure 1: SEM image of FA

2.2. Mineral Carbonation of FA for Carbon Sequestration:

Mineral carbonation is the process of alkaline oxides and hydroxides in suitable materials absorbing ambient CO₂ and converting it to thermodynamically stable carbonates. It is a complicated sequence of chemical and mineralogical changes that occurs during natural rock weathering. It's essentially an acid-base process in which a solid base neutralizes an acid produced by CO₂ dissolving in water (H₂CO₃) (alkaline mineral). Ca and Mg-bearing silicate minerals are carbonated to produce Ca and Mg carbonates under natural ambient conditions. Carbonic acid (H₂CO₃) formed by the reaction of atmospheric CO₂ with rainwater transforms alkaline earth elements to carbonate minerals in this process. The following is a list of the reactions involved in the carbonation mechanism:



2.3. Reaction Temperature:

At ambient temperature, the carbonation reaction with gaseous CO₂ is sluggish, but it speeds up as the temperature rises, since the leaching of Ca from the matrix increases quicker as the temperature rises. At temperatures over 550°C, CaO, for example, has been shown to carbonate on a one-minute time scale. When the temperature is increased too high, however, the solubility of CO₂ in water is reduced because the greater kinetic energy induces more motion in molecules, which breaks the intermolecular bonds between CO₂ and water, allowing CO₂ to leave the solution. The chemical balance is altered in this manner, favoring free CO₂ over the bound version. As a result, bicarbonate activity is reduced at higher temperatures.

2.4. CO₂ partial pressure inside the reactor:

The study results on the impact of CO₂ pressure on the mineralization response seem to be inconsistent, making any trend difficult to discern. However, it is critical to recognize that mineral conversion efficiency and conversion rate are two distinct factors that have been studied. When the partial pressure of CO₂ within the reactor was raised from 2 to 17 bars, the time needed for full carbonation was reduced from nearly 2 days to 3.5 hours, according to Rendek et al [8]. Huijgen et al., on the other hand, discovered that CO₂ partial pressure within the reactor had no impact on the pace of mineralization, indicating that it is the leaching of Ca to the solution, not CO₂ mass transfer, that determines the rate of mineralization [9].

2.5. Solid to Liquid Ratio:

Water is required to enhance the carbonation process, as indicated in the equations for the mechanism (Equations 1-5). Direct gas solid carbonation may occur without water, although at a much slower pace than aqueous carbonation. The overall reaction in aqueous carbonation is a three-step process: Ca is leached from the solid matrix, CO₂ is dissolved in water to produce bicarbonates, and then carbonates are formed. The first of them is thought to be the rate-limiting

phase. Moisture availability affects the availability of Ca and other alkaline cations for the reaction by allowing them to leach out of the solid matrix and form hydroxides in the solution. However, too much water may stymie the process by obstructing CO₂ passage via the pores in the particles. As a result, there is an optimal water level that provides the best rate and efficiency of carbonation.

2.6. FA as a Soil Amendment:

FA incorporation in soil alters the physico-chemical, biological, and nutritional quality of the soil, according to the study literature. FA may change the texture of both sandy and sandy clay soils to loamy, which is better for agricultural usage, thanks to its dominating silt-sized particles. FA's low bulk density also makes it a good additive for increasing the bulk density of soils in a combination. Through cation bridging, the Ca²⁺ from FA promotes flocculation between soil particles and helps to maintain a healthy degree of soil aggregation, especially in clay soils. FA increases water retention capacity in sandy soils and hydraulic conductivity in clay soils due to structural and textural changes in the soil. FA may be used as a soil buffering agent to address excessive acidity or alkalinity in problem soils, depending on its pH. Except for N, FA includes nearly all of the necessary plant nutrients. Furthermore, bringing the pH of problematic soils towards the neutral zone aids in increasing the availability of nutrients in the soil. Researchers that applied FA to agricultural soils saw a rise in plant growth and crop output, which they attribute to improved nutrient availability in the soils and increased accessible water capacity.

2.7. Effect of Accelerated Carbonation on Metal Leach Ability Characteristics Of FA:

Carbonation has been discovered as a method of turning FA into a solid waste material that may be disposed of in landfills. In accelerated carbonation, the ash is treated with CO₂ under enhanced reaction circumstances to create new mineral phases that cause chemical and mineralogical changes that aid in improving the ash's leaching characteristics following the reaction. One of the main modifications influencing better leaching behavior is the formation of carbonate. Metal carbonates, in general, are less soluble than metal oxides and/or hydroxides. As a result, heavy metal immobilization is favored by the conversion of oxides to carbonates. During rapid carbonation, the production of insoluble oxides promotes the immobilization of some inorganic pollutants of concern, such as Pb and Zn. Furthermore, the carbonation process alters the pH of the ash, which helps to minimize the risk of heavy metal leaching. FA has a high alkalinity and metal leachability due to the presence of lime. Accelerated carbonation reduces hazardous metal levels in ash leachate by lowering the pH of alkaline ashes to values matching to the lowest solubility levels of heavy metals, which are usually believed to be pH 7-10, due to its mineralogical modifications. Another reason for metal retention in carbonated ash is metal affinity for newly produced minerals, primarily calcite (CaCO₃). Toxic metals may be absorbed and/or co-precipitated into new minerals, reducing their potential for leaching.

The impact of rapid carbonation on metal leachability of various ashes (fly ash, bottom ash, air pollution control residues) produced by municipal solid waste incineration has received a lot of attention. The impact of pH variations during carbonation on metal mobility has been found by several studies. Metal leachability is mainly determined by the pH of the solution, whether the FA is fresh or carbonated. There are specific metal release curves for several trace elements that

are pH dependent. In order to produce ashes with the least metal leachability, a pH of 9-10.5 has been determined as the optimum pH for the carbonation process based on the trend. In most solution pH ranges, however, carbonated FA has a lower potential for metal leaching than fresh FA for the majority of the elements of concern.

2.8. Effect of Accelerated Carbonation on Alteration of pH And EC of Combustion Residues:

The addition of FA to soil results in substantial increases in pH and EC values. The dissolution of Ca, Mg, and OH ions from FA is responsible for the first rise in pH. The hydration and carbonation processes in FA convert CaO and MgO to more stable secondary mineralogical products (carbonates) over time, stabilizing pH and EC. This stabilization, however, takes many years under typical storage conditions. The fast adsorption of CO₂ into alkaline materials is facilitated by accelerated carbonation, resulting in a pH drop and calcite precipitation. Fernandez Bertos et al. found similar findings when they examined the changes in the pH of MSWI FA before and after carbonation [10]. They discovered that following carbonation reactions, the pH of ashes drops to 8 (near neutral), despite the fact that it was as high as 12 before carbonation. The production of calcites and the reduction of free oxides and hydroxides during rapid carbonation increase the ash's acid neutralization ability, making it more useful for recovering damaged soils. MSWI FA exhibited a considerable buffering capacity between neutral and alkaline values at pH about 7-8 following carbonation treatment, according to Cappai et al [11].

3. CONCLUSION

Coal FA is a hazardous waste that cannot be disposed of in regular landfills. It can be converted to a non-hazardous waste that can be utilized on agricultural land while lowering carbon dioxide levels in the atmosphere via rapid carbonation. Because natural carbonation of alkaline minerals takes geologically long periods, it is necessary to speed up this process by manipulating operating parameters to achieve a successful rate of CO₂ collection and storage. However, there are just a few study results on coal FA carbonation, which makes determining its potential application in CO₂ sequestration difficult. Based on the findings from MSWI ash, optimizing operational parameters such as providing the proper temperature and CO₂ pressure combination, mixing with the water to achieve the best water to solid ratio, and preceding the reaction for a sufficient time period will allow any type of FA to take advantage of the maximum CO₂ sequestration benefit. FA's chemical and mineralogical characteristics are altered after carbonation, making it a good option for soil application. Carbonation aids in the reduction of hazardous metals contained in FA, namely Pb and Zn, leachability. The conversion of alkaline oxides/hydroxides to carbonates lowers the pH of highly alkaline FA to a neutral-slightly alkaline range, which is suitable for soil application. As a result, rapid carbonation of FA followed by its application to agricultural land may be a good way to manage this solid waste. However, owing to a paucity of study data, exact judgments on the potential addition of coal FA to soil are difficult. This highlights the need for further coal FA study in order to determine its potential for CO₂ sequestration and soil addition.

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