

Accelerated Carbonation of Coal Combustion Fly Ash for Atmospheric Carbon dioxide Sequestration and Soil Amendment: An Overview

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Abstract

Fly ash is one of the major solid by-products generated by coal combustion for power generation. At present most fly ash generated all over the world is dumped as waste material without any beneficial use. Only a small proportion of the total fly ash production is used in applications such as cement production, mineral wool production, recovery of metals, road sub-base construction, mine reclamation, and in agriculture. In addition, fly ash is a material that can be used to capture and store atmospheric CO₂ through mineral carbonation both in situ and ex situ of the source of CO₂ emissions. As a means of increasing the rate of mineral carbonation, accelerated carbonation has been researched by scientists in the recent past. In addition to achieving the benefits of carbon sequestration, accelerated carbonation can make the fly ash chemically stable, which is beneficial in overcoming problems associated with the leaching of toxic elements when using it as a soil amendment. Therefore, through accelerated carbonation followed by addition to soil this solid waste material can be successfully managed. The efficacy of the mineralization reaction depends on the mineralogy, and the physical and chemical properties of fly ash and the reaction conditions, such as CO₂ partial pressure, temperature, relative humidity and the contact time of gas and the material. In order to achieve higher CO₂ sequestration efficiency it is vital to select material with the required properties and to supply it with the optimum reaction conditions. This paper reviews the main issues related to the accelerated carbonation of coal combustion fly ash under different reaction conditions and its effects on CO₂ sequestration efficiency. It also identifies the potential application of carbonated fly ash to soil in order to improve soil's physical and chemical properties.

Keywords: Coal fly ash; Accelerated carbonation; CO₂ sequestration; Operational parameters; Soil amendment; Metal leachability

Introduction

Coal is one of the three major fossil fuel resources in the world that are combusted for energy, the other two being oil and natural gas. Coal combustion alone contributes up to 40% of the total global energy and the figures are ever-increasing, due to rising demand for electricity and the availability of coal reserves in many parts of the world. During the combustion of coal two types of ashes are generated: fly ash and bottom ash, in approximate mass fractions of 90% and 10%, respectively [1]. Fly ash (FA) is obtained by the electrostatic or mechanical precipitation of dust-like particles from the flue gas stream [2]. By the year 2000, the total coal FA production of the world was around 600 million tonnes, with only 20% being utilized beneficially, mostly in the cement industry [3]. FA is a rapidly accumulating solid waste material which causes enormous problems for disposal unless a way can be found to utilize it on a large scale.

At the same time, the threat of global warming caused by elevated levels of carbon dioxide (CO₂) in the atmosphere is causing the scientific community to move towards greenhouse gas mitigation technologies [4]. Therefore, a great deal of research is being conducted on the capture and storage (sequestration) of atmospheric CO₂ by various means. The placement of super-critical CO₂ into geological media such as deep oceans, underground coal formations, saline aquifers and depleted oil/gas reservoirs is practised worldwide as a common method of CO₂ sequestration [4-7]. In addition, the accumulation of atmospheric carbon into above ground plant biomass and its addition to the soil organic carbon pool is achieved by the restoration of marginal land to forest [8]. The use of alkaline materials for the sequestration of CO₂ by mineral carbonation is attracting interest among the scientific community as an innovative concept. In mineral carbonation, CO₂ is reacted with minerals to form solid carbonates [9]. This form of sequestration is truly a permanent method since the mineral carbonates

are stable over geological time periods of millions of years, rather than the hundreds to thousands of years of stability expected for other forms of sequestration [10]. 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 the permanent sequestration of CO₂ brings added environmental benefits, by helping to manage these solid wastes in an environmentally-sound manner. In addition, it offers the possibility of trading carbon credits for the incineration companies if mineral carbonation is introduced as a finishing step to incinerator facilities [11,12].

Apart from its applications in the cement and geo-polymer industries, coal combustion FA is attracting attention as a material with the capacity to beneficially alter the properties of soil. Researchers have reported the potential of FA for engineering soils to increase the stability of soil by taking advantage of its self-cementing properties [13,14]. Moreover FA has been shown to have the potential to improve soil's agronomic properties, including moisture- holding capacity and hydraulic conductivity, soil structure and texture, pH buffering capacity and the supply of macro- and micro-nutrients [15]. However, FA is not commercialised as a fertilizer or a soil ameliorant because of the possibility of contamination of soil and ground water

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at high dosages by the hazardous trace elements present in it and the undesirable pH changes caused by the addition of some FAs [16]. Therefore, pre-treatments are usually recommended before applying FA to soils to leach out toxic elements and to adjust its pH. According to Pandey and Singh [17] weathering helps to reduce the leachability of toxic elements, especially boron (B), after the addition of FA to soil. Nevertheless, it can contaminate ground water resources at dump sites. The addition of carbonated FA to soil may present a better option, since the carbonation reaction is proven to alter the chemical stability of ashes and improve their leaching behaviour. In addition, carbonation reduces the alkaline pH of the ashes to a range that is suitable for soil application. The mineral carbonation of FAs occurs naturally when they are exposed to atmospheric CO₂ and moisture in collection ponds. However, this natural carbonation reaction which mimics rock weathering takes geological times to complete [18]. Therefore, the CO₂ uptake efficiency under natural carbonation is very much slower to achieve FA carbonation and atmospheric CO₂ removal rates comparable to the emission rates. Accelerated carbonation with enhanced reaction conditions has the potential to reduce the time required for carbonation down to hours or days [12]. Therefore, it appears to be a viable approach to the capture and storage atmospheric CO₂ in a stable form.

This paper reviews studies of the accelerated carbonation of coal combustion FA under different reaction conditions to identify its CO₂ sequestration potential. Furthermore, it discusses the benefits of accelerated carbonation of FA prior to its use as a soil amendment.

Properties of Coal Combustion FA

FA is the portion of ash produced by coal combustion which has sufficiently small particle size to be carried away from the boiler in the flue gas [19]. It is a complex heterogeneous material with an amorphous (glassy) structure with possibly some crystalline phases [20,21]. The primary components of the FA matrix are silica (SiO₂), alumina (Al₂O₃) and iron oxides (Fe₂O₃) [22]. It also contains small contents of quartz, mullite, hematite and magnetite as the major mineral phases [23].

The mineralogical, physical and chemical properties of FA vary, depending on the type of coal burned, boiler type, collector set-up, and the efficiency of the collectors [24]. Therefore, the ashes produced by the burning of bituminous, anthracite and lignite coals have different compositions [25]. Generally two classes of FA can be identified: (a) Class F and (b) Class C, depending on the amounts of calcium, silica, alumina and iron content in ash coming from the parental coal. Class C FA is produced by burning lignite or sub-bituminous coal and generally contains more than 20% lime (CaO). These ashes show a self-cementing effect called pozzolonic activity, which is primarily governed by the CaO content. Burning of harder and older anthracite and bituminous coals produces Class F FA, which contains less than 10% lime [26].

FA particles are very fine in texture with a grain size distribution of sandy silt to silty loam. Particle diameter can range between 0.01–100 μm but most particles in a sample are 2–20 μm, belonging to the silt-sized range [27]. Morphologically, FA is usually characterized as spherical non-opaque with a surface area range of about 1 m²/g. The spheres can be solid, hollow, irregularly shaped, or filled with smaller spheres [24]. Figure 1 shows a scanning electron micrograph (SEM) of a FA sample showing its typical spherical morphology and size range.

FA has a light texture and a low to medium bulk density varying from 1 to 1.8 gcm⁻³ [27-29]. It has dielectric property (dielectric constant, 104) and can be used in electronic applications [26]. The

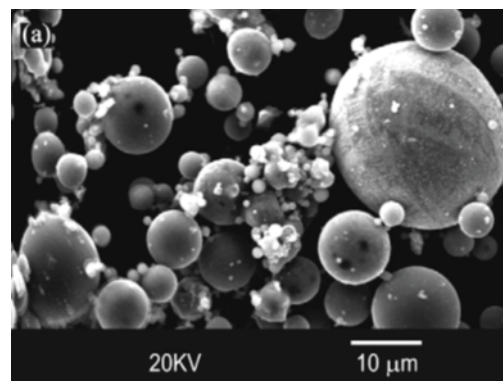


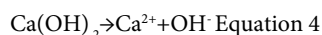
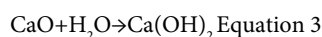
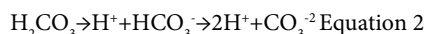
Figure 1: SEM image of FA [27].

chemical properties and composition provide the greatest variability in FA. Chemically, 90-99% of FAs consist of Si, Al, Fe, Ca, Mg, Na, with K forming the major matrix [27]. It is also rich in trace elements like As, B, Mo, S, Se, Cd, Pb, Zn, Co and Hg [25]. The high level of soluble salts and heavy metals present in some FAs make them a hazardous waste material which cannot be directly deposited into landfills [11]. According to Adriano, et al., [30] most of these heavy metals are concentrated into smaller ash particles. It is reported that the amounts of organic carbon and nitrogen are low in FAs since they tend to oxidise during coal combustion [31]. The variable amount of unburned carbon present in FA gives it a colour ranging from grey to black [32]. FA can have a pH from 4.5 to 12, depending largely on the S, Ca and Mg content of the parental coal [16], but most FAs produced worldwide are alkaline because of the presence of hydroxides and carbonate salts of Ca and Mg [27,33]. The high content of soluble salts gives FA the values of the electrical conductivity of saturated extracts ranging from 0.63 to 55 dS/m [33].

There is a great variation in the properties of coal FAs, as discussed above. It is therefore vital to select FA with the required characteristics before using it as a candidate material for any application, including carbon capture and storage and soil amendment.

Mineral Carbonation of FA for Carbon Sequestration

Mineral carbonation involves the uptake of atmospheric CO₂ by alkaline oxides and hydroxides present in the candidate materials to form thermodynamically stable forms of carbonates [34,35]. It is one of the steps in natural rock weathering which comprises a complex series of chemical and mineralogical transformations [36]. Basically, it is an acid base reaction where an acid formed by dissolution of CO₂ in water (H₂CO₃) is neutralised by a solid base (alkaline mineral). Under natural ambient conditions, Ca and Mg-bearing silicate minerals are carbonated to form Ca and Mg carbonates. In this process, the carbonic acid (H₂CO₃) which results from the interaction of atmospheric CO₂ with rain water converts the alkaline earth materials into carbonate minerals [37]. The sequence of reactions involved in the carbonation mechanism can be written as follows:



Naturally-existing primary minerals such as wollastonite (CaSiO_3) and olivine (Mg_2SiO_4) are suitable to be used as feedstock for mineral CO_2 sequestration [38]. The theoretical maximum CO_2 uptake capacity of such silicate materials can be estimated as a function of their chemical composition, although the actual capacity may vary, depending on the availability of oxides for reaction and the presence of certain components which might influence the effective diffusivity and reactivity of CO_2 [5]. The carbonation of industrial wastes and by-products which contain significant amounts of calcium and magnesium that can be carbonated has received growing attention as a means of permanent CO_2 sequestration over the past decade. Although the total sequestration capacity of wastes is limited compared to primary minerals, the use of alkaline solid wastes facilitates cost-effective ways of CO_2 sequestration and provides environmental benefits by managing wastes usefully [34]. In addition, these residues tend to be more reactive in carbonation due to their chemical instability, whereas in minerals the surface needs to be activated either by physical or chemical pre-treatment methods in order to increase the effective carbonation yield [10,12,34]. Table 1 presents a list of various alkaline solid wastes that are being researched for their potential use as feedstock for mineral CO_2 sequestration.

From the current research literature, it is clear that coal FA has been drawing most attention as a material that can be used for mineral carbon sequestration. The potential of FA for mineral sequestration depends directly on the proportion of alkaline (Ca, Mg) oxides and/or hydroxides present in the FA matrix [28]. In FA, CaO may occur as both free lime and embedded in glassy spheres. Glassy spheres are formed from the reaction of free lime with SO_2 , or from free lime and aluminosilicate melt, and reduce the availability of CaO for carbonation [39]. Since different FAs contain varying amounts of available oxides for carbonation, they show varying capacities to capture and store CO_2 . An experimental study using FA containing 4.1 wt% of CaO demonstrated that one tonne of FA can sequester up to 26 kg of CO_2 [28]. According to Nayambura et al. [39] one tonne of bulk FA with 9.2 wt% of CaO carbonated in a brine solution sequestered up to 62.35 kg of CO_2 .

The energy consumption and costs of carbon sequestration through mineral carbonation is limited by the exothermic nature of the carbonation reaction [34]. Therefore, this method provides a promising route for reducing the atmospheric CO_2 on a large scale. In addition, this is the only CO_2 sequestration option available for countries where large deep underground reservoirs do not exist and ocean storage of CO_2 is not feasible [48]. Their low cost and the widespread availability of FAs in industrial areas are two other advantages of using FA as a feedstock for CO_2 sequestration. However, the natural weathering process under ambient conditions proceeds too slowly [12], and only becomes significant in the long term. Hence, natural weathering cannot contribute to the effective mitigation of global warming. Therefore, mineral sequestration aims to accelerate the reaction to obtain a viable industrial process [34].

Accelerated carbonation

In accelerated carbonation, the natural reactions occurring during

Alkaline solid waste material	References
Coal fly ash	[27,36,38]
Bottom ash	[39-41]
MSWI ash	[5,11,42,43]
Air pollution control residues	[34,44]
Steel slag	[33,45]
Oil shale solid residues	[46,47]

Table 1: Potential alkaline solid wastes as a feedstock for mineral carbonation.

rock weathering are accelerated by various means in order to reduce the time required for complete carbonation down to time-scales of hours or days [11,12]. It helps to effectively manage the excessive amounts of CO_2 produced by some industries such as coal combustion and municipal solid waste incineration using the alkaline solid residues generated in the same sites. However, the widespread practical use of this technology has been limited by the factors such as the requirement to separate CO_2 from the flue gas stream, the compression of CO_2 , and the transportation or safe storage of CO_2 if needed [37].

The efficiency of the mineral carbonation reaction will depend on the mineralogy, and the chemical and physical properties of the candidate material and the operational parameters governing the carbonation process. Typically, in accelerated carbonation the mixture is carbonated in a gaseous CO_2 rich environment [5]. The partial pressure of CO_2 inside the reactor is identified as one of the parameters that influence the rate and the efficacy of the carbonation process [39]. In addition, researchers have been experimenting to optimize other process conditions such as the reaction temperature, the moisture content of the mixture, the contact time with the gas and the provision of adequate mixing between the gas and the material in order to achieve an efficient mineral carbonation process [5]. The effects of these parameters on the carbonation of fly ash can be evaluated from the findings available in the research literature which is discussed below.

Reaction temperature

The carbonation reaction with gaseous CO_2 proceeds very slowly at atmospheric temperature and accelerates with increased temperature, since the leaching of Ca from the matrix becomes faster with increased temperature [38]. For example, CaO has been found to be carbonated on a time-scale of one minute at temperatures above 550°C [49]. However, if the temperature is raised too much, the solubility of CO_2 in water is lowered since the higher kinetic energy causes more motion in molecules which breaks the intermolecular bonds between CO_2 and water, and allows CO_2 to escape from the solution [50-53]. In this way, the chemical equilibrium is shifted such that free CO_2 is favoured over the bound form. Therefore, at higher temperatures bicarbonate activity is low [18].

As a result, the temperature inside the reactor can only be increased up to a certain level before the formation of CO_2 is favoured over carbonates. This highest allowable temperature that still allows spontaneous binding of CO_2 is a function of the partial pressure of the CO_2 in the reactor [18,22]. For example, at CO_2 pressures of 1 bar MgCO_3 is stable up to temperatures of around 400°C and at 35 bars CO_2 , MgCO_3 is stable up to around 550°C [22]. Therefore, simply increasing the temperature until reaction rates are sufficiently fast would not work without sufficient pressurisation. Nyambura et al. [39] tested the carbonation efficiency of coal FA at two temperatures (30°C and 90°C) and concluded that there was no significant effect of temperature on reaction efficiency. At each temperature they observed the necessity of a high pressure of 4 MPa (over 1 MPa) to achieve high carbonation efficiencies. In a study of aqueous wollastonite (a primary mineral) carbonation Huijgen et al. [23] observed an increase in the rate of carbonation with reaction temperatures between 25 and 150°C at a pressure of 20 bars [38]. However, after 200°C the conversion rate of mineral into carbonate reduced due to the lowered activity of bicarbonate in water. Li et al. [34] carbonated six different types of MSWI ash under a temperature range of 21-91°C at a pressure of 3 bars and concluded that the higher temperature improves the reaction velocity but does not improve the sequestration of CO_2 into the ash [11].

CO₂ partial pressure inside the reactor

The research findings on the effect of CO₂ pressure on the mineralization reaction appear contradictory, making it difficult to identify any trend. However, it is vital to understand that the conversion efficiency of the minerals and the conversion rate are two different aspects that have been researched. According to Rendek et al. [54], the time required for complete carbonation to be achieved decreased from over 2 days to 3.5 hours when the partial pressure of CO₂ inside the reactor was increased from 2 to 17 bars [40]. In contrast Huijgen et al. [23] found an insignificant effect of CO₂ partial pressure inside the reactor on the rate of mineralization pointing out that CO₂ mass transfer is not rate-determining but the leaching of Ca to the solution [38].

Montes-Hernandez et al. [41] showed that the degree of carbonation of CaO was independent of the pressure of CO₂ and they therefore suggested a moderate pressure (10 bars) system for ex situ industrial level carbonation [27]. However, the initial rate of CO₂ transfer (sequestration rate) increased linearly with the pressure from 10 to 40 bars, as shown in Figure 2.

The research literature does not provide any evidence to clearly identify the effect of CO₂ pressure on the overall efficiency of the conversion of minerals into stable carbonates. Instead, CO₂ partial pressure has been found to have an influence on the optimum reaction temperature [12].

Solid to liquid ratio

As shown in the equations for the carbonation reaction mechanism (Equations 1-5), water is necessary to promote the reaction. Without water, direct gas solid carbonation may occur, but at a very slow rate compared to aqueous carbonation [12]. In aqueous carbonation the overall reaction occurs as a three-step process: the leaching of Ca from the solid matrix; the dissolution of CO₂ in water to form bi-carbonates; followed by the formation of carbonates. Of these, the first step is considered to be the rate-limiting step [10,12]. The moisture availability influences on making Ca and other alkaline cations available for the reaction by leaching them out to the solution from the solid matrix and forming the hydroxides. However, too much water can hinder the reaction by lowering the diffusion of CO₂ due to the blockage of the pores in the solids [5]. Therefore, there is an optimum level of water which gives the maximum rate and efficiency of carbonation.

The sequestration potential of CO₂ by alkaline materials is generally measured as the percentage dry weight gain after the carbonation

reaction [12]. Figure 3 compares the outcomes of several studies of the effect of the moisture-to-solid ratio on the mineralization efficiency of alkaline wastes, based on the percentage dry weight gain after the reaction.

According to the figure, all three types of MSWI ash show their maximum weight gain percentages at a 0.2-0.3 moisture-to-liquid ratio. At this moisture level, the mixture is more or less a solid. However, for materials of low solubility in which CaO is bound as silicates, the accelerated carbonation is best carried out in a slurry phase with a liquid-to-solid ratio of greater than one [38,51]. Reddy et al. [53] examined the possibility of point-source capture of the flue gas CO₂ with coal FA generated in the same plant [37]. They found that the moisture content of the flue gas is the most important factor that governs the mineralization of the FA particles. A moisture content of 16% in flue gas gave the highest conversion efficiency of CO₂ to carbonates.

In addition to the operational parameters discussed above, the contact time of reactants, particle size of the residue materials, provision of stirring and speed of mixing influence the aqueous mineralization of waste materials [5,38,39,44]. The evaluation of the up to date research findings regarding the effect of these parameters on the rate and the efficiency of the sequestration reaction does not allow drawing generalized conclusions but appears to be depended on the residual composition and several other situation specific conditions.

FA as a Soil Amendment

The research literature provides substantial evidence that FA incorporation in soil modifies the physico-chemical, biological and nutritional quality of the soil. With its dominant silt- sized particles, FA can alter the texture of both sandy and sandy clay soils to loamy, which is favourable for agricultural use [52]. In addition, the low bulk density of FA makes it a suitable additive to improve the bulk density of soils in a mixture [19]. The Ca²⁺ from FA promotes flocculation between soil particles and helps to maintain a desirable level of soil aggregation through cation bridging, particularly in clay soils [29,53]. The structural and textural changes in soil upon FA addition increase water retention capacity in sandy soils and hydraulic conductivity in clay soils [22,31,54]. Depending on its pH, FA can be used as a soil buffering agent to correct extreme acidity or alkalinity in problem soils [29]. FA contains almost all the essential plant nutrients except N [27]. In addition, the adjustment of the pH of problem soils into the neutral range helps increase the availability of the nutrients in the soil [55]. Researchers who added FA to agricultural soils have observed increased plant growth and crop production, which can be principally

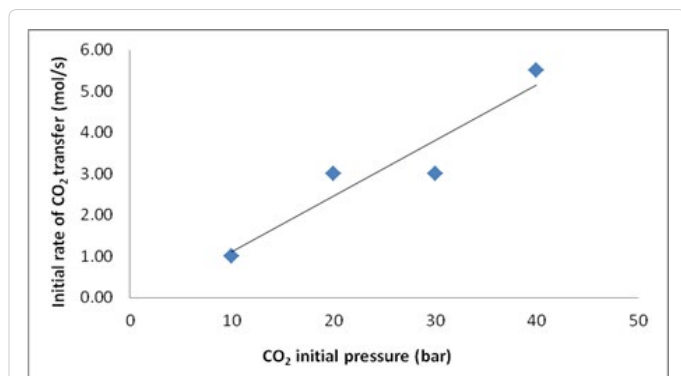


Figure 2: Linear increase of initial rate of CO₂ transfer with CO₂ initial pressure.

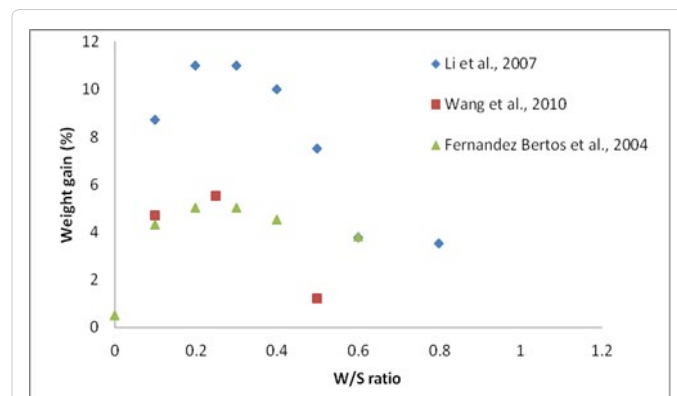


Figure 3: Effect of water-to-solid (w/s) ratio on carbonation efficiency.

attributed to the enhancement of nutrient availability in soils and the improvement of available water capacity [15,21,56].

However, some problems are associated with the continuous use of FA, particularly unweathered ash, as a soil ameliorant. The primary concern is the potential leaching of hazardous metals into the soil from some FAs, especially when applied at high rates [57]. FA contains some biologically toxic elements in concentrations that greatly exceed their concentrations in soil [16,31]. Table 2 compares the concentration ranges of some of those elements of interest in FA and soil.

Continuous loading of soils with FA therefore leads to a tendency to accumulate these elements leached from the FA matrix into the soil. From the soil they can be taken up by vegetation or percolated into the ground water sources and cause serious contaminations [31]. Trace elements are persistent global pollutants and accumulation up to toxic levels of these elements is responsible for reductions in crop yields, leading to negative consequences for animal and human health [58,59]. The toxicity of B is one of the major limiting factors in the agricultural use of FA [16].

Another concern with FA addition to soil is related to the changes caused in soil pH and salinity. The pH of FA can be acidic or alkaline, depending on the source. Accordingly, FA is being used as a buffering agent to reclaim problem soils with undesirable alkalinity or acidity [29]. However, since most of the FAs produced worldwide have strong alkalinity in the pH range of 8 to 12, their addition as a soil ameliorant into agricultural soils can bring about unfavourable changes to soil pH [16]. This can then lead to increased bioavailability of some trace metals to levels that are toxic for plants and animals. For example, Riehl et al. [55] observed an increase in soil pH from 8.1 to 12 in calcareous soils amended with alkaline coal FA, which ultimately caused the mortality of soil micro fauna and increased mobility of Co, Ni and V [60].

The development of salinity in soils with added FA has limited its environmentally-beneficial final disposal. Salinity is a measure of the soluble salt content of a material which helps to conduct electricity in a solution and is therefore measured and expressed in units of electrical conductivity (EC). Increased salinity in soils created by added FA is attributed to the high levels of soluble salts of Ca, Mg, Na and B present in it [29]. According to Page and Elsiwee [58], FA from Nevada power plants increased soil salinity by 500 to 600% and caused a significant increase in soluble B, Ca, and Mg levels in soil. The development of salinity in soil can induce salt stress in plants and reduce plant growth and yield [61].

Owing to the above limitations, coal FA, particularly which has

Element	Concentration range in fly ash (µg/g)	Concentration range in soil (µg/g)
As	2.3-6,300	0.1-40
B	10-618	2-100
Cd	0.7-130	0.01-7.0
Cr	10-1,000	5-3,000
Cu	14-2,800	2-100
Mn	58-3,000	100-4,000
Mo	7-160	0.2-5.0
Ni	6.3-4,300	10-1,000
Pb	3.1-5,000	2-100
Rb	36-300	30-600
Se	0.2-134	0.1-2.0
Zn	10-3,500	10-300

Table 2: Elemental composition of FA and soil [58].

not undergone any ageing or pre-treatment, should be added to soil with special care. The dosage of FA that can be added to the soil with no potential deleterious effect on soil, plants or animals needs to be pre-determined before large-scale applications are carried out. The application of FA in conjunction with other bio solids such as sewage sludge, compost, poultry manure and blue green algae helps to reduce the detrimental effects by stabilizing the potentially toxic metals and increasing the pH buffering potential of coal FA [62-67]. Moreover, the treatment of fly ash prior to soil application can be practised to leach out the harmful elements. According to Pandey and Singh [17] careful weathering of FA helps to overcome the problem of B toxicity by reducing the B availability in FA to below toxic levels. In addition, washing is done to remove the contaminants present in FA. In this process, water or acid is used as the solvent to dissolve most of the hazardous chemicals and the soluble salts. The generation of large amounts of water is the main disadvantage of this method [68].

Similarly, the problems caused with soil pH and salinity by the addition of FA is affected by the extent to which it is weathered. Therefore lagooning, leaching and stockpiling are considered as minimizing the ill-effects of unweathered FA, and making it more suitable for soil addition [58]. In addition, the mixing of FA with other soil ameliorants is done to adjust its pH. For example, mixing alkaline FA with highly carbonaceous acidic materials is recommended to make compost for soil treatment [30]. Accelerated carbonation can also be used as a treatment method capable of improving the environmental and technical behaviour of different types of combustion residues [69]. The chemical and mineralogical transformations which occur during carbonation can alter the properties of FA to make it more favourable for soil application. However, very few research findings are available on the effect of accelerated carbonation on the chemical stability of coal combustion FAs, and this does not allow a clear picture of any beneficial effects to be drawn. Therefore, the scenario for MSWI ashes was used to visualize how well accelerated carbonation can contribute to changing the leaching characteristics and pH of combustion residues, even though MSWI ashes are more toxic and more problematic than coal combustion residues. The following sub-section discusses this issue in detail.

Effect of accelerated carbonation on metal leach ability characteristics of FA

As mentioned above, the ashes generated from coal combustion and municipal solid waste incineration are generally contaminated with toxic heavy metals, which tend to leach out in contact with water [70]. The extent of trace metal leaching from any solid waste material depends on the chemical species of the element, the bonding of the elements to the material, the solubility and diffusivity of element species, and the pH of the make-up water [56]. In FAs the toxic elements accumulate in a thin layer (<1000 Å) at the particle surface and therefore they may be more readily leached in water than other ash constituents [59]. With regard to pH, acidic FAs leach out almost all metals into water except B and Se, while alkaline FAs are responsible for releasing B, Ba, As, Cr, Cu, Ni, Se and Zn into water, of which some (B, Ba, Cr, Se) are of special concern as they often exceed the toxic limits set out in environmental regulations [59,71].

The process of carbonation has been identified as a way of converting FA into a solid waste material which may be allowable for disposal in landfills. In accelerated carbonation, the ash is treated with CO₂ under improved reaction conditions to produce new mineral phases which are responsible for bringing about chemical and mineralogical changes which help to improve the leaching properties

of the ash after the reaction [11,41,42]. Formation of carbonate is one of the major changes affecting improved leaching behaviour. Generally, metal carbonates are less soluble than metal oxides and/or hydroxides. Therefore, the conversion of oxides into carbonates favours heavy metal immobilization [69]. At the same time, the formation of insoluble oxides during accelerated carbonation causes the immobilisation of certain inorganic contaminants of concern such as Pb and Zn [72]. In addition, the changes in ash pH caused by the carbonation process, helps to reduce the potential for leaching of heavy metals. The presence of lime gives FA high alkalinity and increased metal leachability. Through its mineralogical changes, accelerated carbonation decreases the pH of alkaline ashes to values corresponding to the minimum solubility levels of heavy metals, which are generally considered as pH 7-10, and thus is responsible for reducing toxic metal levels in the ash leachate [5,11,71]. Another metal retention mechanism in carbonated ash is based on the affinity of metals to the newly-formed minerals, mainly calcite (CaCO_3). Sorption and/or co-precipitation of toxic metals into new minerals can reduce their potential for leaching [42,69].

A great deal of research has focussed on the effect of accelerated carbonation on metal leachability of different ashes (fly ash, bottom ash, air pollution control residues) generated by municipal solid waste incineration. Many researchers have discovered the importance of pH changes during carbonation for the influence on metal mobility [5,11,69,73]. Whether the FA is fresh or carbonated, its metal leachability is largely governed by the solution pH [74]. For many of the trace elements there are characteristic metal release curves which depend on the pH. Based on the trend, a pH of 9-10.5 have been identified as the best pH for the carbonation reaction in order to obtain ashes with least metal leachability [44,69]. However, in most solution pH ranges carbonated FA shows a reduced potential for metal leaching compared with fresh FA for most of the elements of concern.

Particularly Pb and Zn leachability have been found to decrease significantly after carbonation. In many of the fresh ashes, Pb and Zn are present above the landfill acceptance value of 50 mg kg^{-1} . However, after carbonation these figures are reduced to levels lower than 1 mg kg^{-1} [5]. Figures 4a and 4b shows the reduction of Pb and Zn leachability after the accelerated carbonation of 12 different types of ashes (MSWI and Coal FAs).

According to the Figure 4, almost all the ashes show markedly reduced leaching potential of Pb and Zn after the carbonation. Cappai et al. [9] observed a reduction of Cu release by 2 orders of magnitude after the carbonation of MSWI ash. Furthermore, the mobility of both Cr and Mo reduced by one order of magnitude.

In their experiments on supercritical fluid extraction with CO_2 for MSWI ash, Kersch et al. [30] observed successful reductions in leachability of Zn, Pb and Mn. Super-critical fluid extraction is a promising method to reduce the extent of metal leachability of hazardous wastes [70]. In this process the use of CO_2 as the extracting fluid is attractive because of its high diffusivity and low viscosity which allow easy penetration into the smallest pores of particles such as FA. In accelerated carbonation, CO_2 may play a similar role in immobilizing the toxic metal levels of ashes.

Effect of accelerated carbonation on alteration of pH and EC of combustion residues

The addition of FA to soil produces significant increases in the levels of pH and EC. The initial increase of pH is attributed to the dissolution of Ca, Mg and OH ions from FA [74]. With time the hydration and

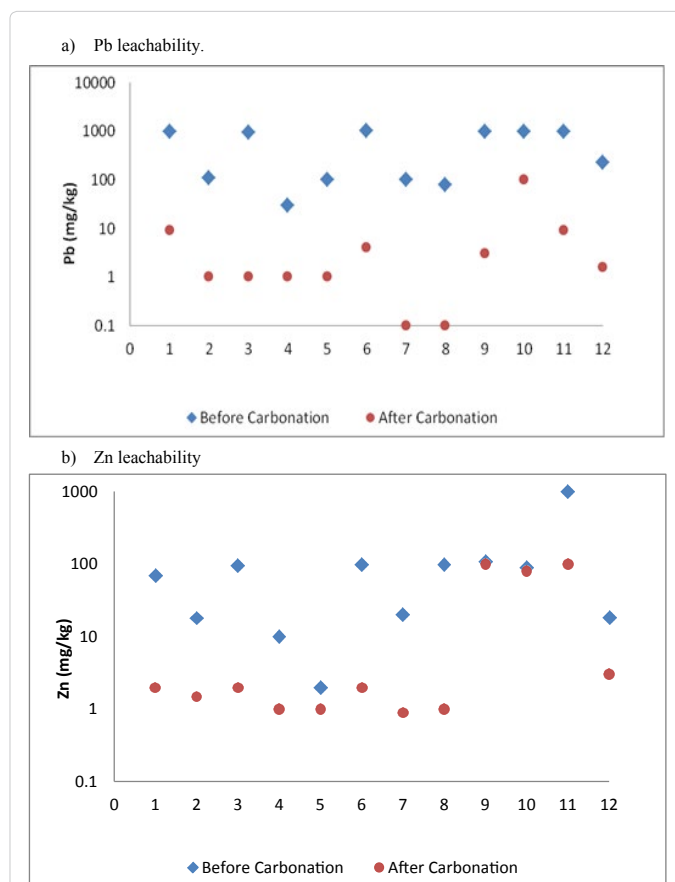


Figure 4: Metal release of different types of fresh and carbonated ashes [5,11,69].

carbonation reactions transform CaO and MgO in FA to more stable secondary mineralogical products (carbonates), and as a result pH and EC are stabilized. However, under normal storage conditions this stabilization takes several years [59]. Accelerated carbonation facilitates the rapid adsorption of CO_2 into alkaline materials which causes pH decrease and calcite precipitation. Li et al. [34] observed a lowering of the pH of fresh MSWI fly ash from 12-12.5 to 7-10 after accelerated carbonation. Similar results are reported by Fernandez Bertos et al. [20] that compared the changes in the pH of MSWI FA before and after carbonation [5]. They concluded that the pH of ashes falls below 8 (nearly neutral) after carbonation reactions take place, although it was as high as 12 before carbonation. The decrease in free oxides and hydroxides and the formation of calcites during accelerated carbonation improve the acid neutralization capacity of the ash which enhances its use in reclaiming problem soils [72]. According to Cappai et al. [9] MSWI FA showed a significant buffering capacity between neutral and alkaline values at pH around 7-8 after carbonation treatment [69].

Similar to the rise in pH, FA not subjected to any pre-treatment increases soil salinity (EC) due to the high level of soluble salt present in it. Carbonation can alter the EC of FA through the same mechanism which neutralizes its pH. The reduced leachability causes fewer solutes in the soil solution after the application of carbonated ashes into soil and thus it controls the raising of soil salinity.

Conclusion

Coal FA is a hazardous waste material which cannot be directly put

into landfills. Through accelerated carbonation it can be recovered to a non-hazardous waste that has the potential to be used on agricultural land while reducing the elevated levels of atmospheric carbon dioxide. Since the natural carbonation of alkaline minerals takes geological times to complete, the acceleration of this process through the manipulation of operational parameters is required to obtain a successful rate of CO₂ capture and storage. However, only a handful of research findings are available on coal FA carbonation, which limits the identification of its potential use in CO₂ sequestration. Based on findings on MSWI ash, the optimization of operational parameters including supply of proper temperature and CO₂ pressure combination, mixing with the water to the best water to solid ratio and preceding the reaction to sufficient time duration will allow the harnessing of the maximum advantage of CO₂ sequestration for any given type of FA. After carbonation, the alteration of chemical and mineralogical properties in FA makes it a suitable candidate for soil application. Carbonation helps to reduce the leachability of toxic elements present in FA, mainly Pb and Zn. The conversion of alkaline oxides/hydroxides into carbonates also reduces the pH of extremely alkaline FA to the neutral-slightly alkaline range which is acceptable for soil addition. Hence, the accelerated carbonation of FA followed by its use on agricultural land could provide a beneficial route for the management of this solid waste. However, precise conclusions on the possible addition of coal FA to soil are impossible due to the lack of research evidence. This indicates the need for future research on coal FA in order to identify its possible use for CO₂ sequestration and soil addition.

References

1. Adriano DC, Brisbin IL, Woodford TA, Ciravolo TG (1978) Growth and elemental composition of corn and bean seedlings as influenced by soil application of coal ash. *J Environ Qual* 7: 416-421.
2. Ahmaruzzaman M (2010) A review on the utilization of fly ash. *Prog Energy Combust Sci* 36: 327-363.
3. Arickx S, De Borger V, Gerven TV, Vandecasteele, C (2010) Effect of carbonation on the leaching of organic carbon and copper from MSWI bottom ash. *Waste Manage* 30: 1296-1302.
4. Baciocchi R, Costa G, Poletti A, Pomi R, Di Bartolomeo E, et al. (2007) Leaching behaviour and CO₂ sequestration capacity of accelerated carbonated MSWI APC residues. Sardinia 2007 International waste management and landfill symposium, Italy.
5. Baciocchi R, Poletti A, Pomi R, Prigiobbe V, Nikulshina V, et al. (2006) CO₂ sequestration by direct gas solid carbonation of air pollution control (APC) residues. *Energy Fuels* 20: 1933-1940.
6. Behera RK, Naik HK (2010) Characterization of fly ash for their effective management and utilization. Bachelor of Technology Department of Mining Engineering, Thesis. National Institute of Technology, Rourkela, Orissa. pp: 61.
7. Bergeson KL, Pitt JM, Demirel T (1985) Increasing cementitious products of a class C fly ash. *Transp Res Rec* 998: 41-46.
8. Bhatia SK, Perlmutter DD (1983) Unified treatment of structural effects in fluid-solid reactions. *AIChE J* 29: 281-289.
9. Cappai G, Cara S, Muntoni A, Piredda M (2011) Application of accelerated carbonation on MSW combustion APC residues for metal immobilization and CO₂ sequestration. *J Hazard Mater* 207-208: 159-164.
10. Chimenos JM, Fernández AI, Nadal R, Espiell F (2000) Short-term natural weathering of MSWI bottom ash. *J Hazard Mater* 79: 287-299.
11. Costa G, Baciocchi R, Poletti A, Pomi R, Hills C, et al. (2007) Current status and perspectives of accelerated carbonation processes on municipal waste combustion residues. *Environ Monit Assess* 135: 55-75.
12. Da Costa JCD, Prasad P, Pagan RJ (2004) Modern environmental improvement pathways for the coal power generation industry in Australia. *Process Saf Environ* 82: 191-199.
13. Daniels WL, Stewart B, Haering K, Zipper C (2002) The potential for beneficial reuse of coal fly ash in southwest Virginia mining environments. *Powell River Project* 19: 460-134.
14. Dudas MJ, Warren CJ (1987) Submicroscopic model of fly ash particles. *Geoderma* 40: 101-114.
15. Essington ME (1991) Laboratory weathering of combusted oil shale. *J Environ Qual* 20: 794-801.
16. Elseewi AA, Straughan IR, Page AL (1980) Sequential cropping of fly ash-amended soils: effects on soil chemical properties and yield and elemental composition of plants. *Sci Total Environ* 15: 247-259.
17. Pandey VC, Singh N (2010) Impact of fly ash incorporation in soil systems. *Agri Ecosyst Environ* 136: 16-27.
18. Fail JL, Wochoc ZS (1977) Soybean growth on fly ash amended strip mine spoils. *Plant Soil* 48: 473-484.
19. Fernandez Bertos M, Li X, Simons JR, Hills CD, Carey PJ (2004) Investigation of accelerated carbonation for the stabilisation of MSW incinerator ashes and the sequestration of CO₂. *Green Chem* 6: 428-436.
20. Ferreira C, Ribeiro A, Ottosen L (2003) Possible applications for municipal solid waste fly ash. *J of Hazard Mater* 96: 201-216.
21. Feurborn HJ (2005) Coal gas utilization over the world and in Europe. International workshop on Environmental and health aspects of coal ash utilization: European Coal Combustion Products Association Tel-Aviv, Israel.
22. Huijgen WJJ, Witkamp GJ, Comans RNJ (2005) Mineral CO₂ sequestration by steel slag carbonation. *Environ Sci Technol* 39: 9676-9682.
23. Huijgen WJJ, Witkamp GJ, Comans RNJ (2006) Mechanisms of aqueous wollastonite carbonation as a possible CO₂ sequestration process. *Chem Eng Sci* 61: 4242-4251.
24. Iyer RS, Scott JA (2001) Power station fly ash-A review of value-added utilization outside of the construction industry. *Resour Conserv Recycl* 31: 217-228.
25. Izquierdo M, Querol X (2011) Leaching behaviour of elements from coal combustion fly ash: An overview. *Int J Coal Geol* 94: 54-66.
26. Jala S, Goyal D (2006) Fly ash as a soil ameliorant for improving crop production-A review. *Biores Technol* 97: 1136-1147.
27. Jiang RF, Yang CG, Su DC, Wong JWC (1999) Coal fly ash and lime stabilized bio solids as an ameliorant for Boron deficient acidic soils. *Environ Technol* 20: 645-659.
28. Kaszuba JP, Janecky, DR, Snow MG (2003) Carbondioxide reaction process in a model brine aquifer at 200°C and 200 bars : Implications for geological sequestration of carbon. *Appl Geochem* 18: 1065-1080.
29. Kersch C, Peretó Ortiz S, Woerlee GF, Witkamp GJ (2004) Leachability of metals from fly ash: Leaching tests before and after extraction with supercritical CO₂ and extractants. *Hydrometallurgy* 72: 119-127.
30. Kishor P, Ghosh AK, Kumar D (2010) Use of fly ash in agriculture: A way to improve soil fertility and its productivity. *Asian J of Agri Res* 4: 1819-1894.
31. Lackner KS, Wendt CH, Butt DP, Joyce EL, Sharp DH (1995) Carbondioxide disposal in carbonate minerals. *Energy* 20: 1153-1170.
32. Lal R (2004) Soil carbon sequestration to mitigate climate change. *Geoderma* 123: 1-22.
33. Lee H, Ha HS, Lee CH, Lee YB, Kim PJ (2006) Fly ash effect on improving soil properties and rice productivity in Korean paddy soils. *Biores Technol* 97: 1490-1497.
34. Li X, Fernandez Bertos M, Hills CD, Carey PJ, Simon S (2007) Accelerated carbonation of municipal solid waste incineration fly ashes. *Waste Manag* 27: 1200-1206.
35. Mackiewicz SM, Ferguson EG (2005) Stabilization of soil with self cementing coal ashes. World of coal ash (WOCA) Lexington, Kentucky, USA.
36. Malhotra VM (1999) Making concrete greener with fly ash. *Concrete International* 21: 61-66.
37. Matsi T, Keramidias VZ (1999) Fly ash application on two acid soils and its effect on soil salinity, pH, BP and on ryegrass growth and composition. *Environ Pollut* 104: 107-112.
38. Meima JA, Eeijden VRD, Eighmy TT, Comans RNJ (2002) Carbonation process

- in municipal solid waste incinerator bottom ash and their effect on the leaching of copper and molybdenum. *Appl Geochem* 17: 1503-1513.
39. Mitra BN, Karmakar S, Swain DK, Ghosh BC (2005) Fly ash-A potential source of soil amendment and a component of integrated plant nutrient supply system. *Fuel* 84: 1447-1451.
40. Montes-Hernandez G, Pérez-López R, Renard F, Nieto JM, Charlet L (2009) Mineral sequestration of CO₂ by aqueous carbonation of coal combustion fly-ash. *J Hazard Mater* 161: 1347-1354.
41. Muduli SS, Nayak BD, Dhal NK (2009) Impact of climate change on agriculture. In Panigrahy S, Ray SS, Parihar JS (eds) ISPRS Ahmedabad workshop, Ahmedabad, India: Space Application Center, India.
42. Mulder E (1996) Pre-treatment of MSWI fly ash for useful application. *Waste Manag* 16: 181-184.
43. Nyambura MG, Mugeru WG, Felicia PL, Gathura NP (2011) Carbonation of brine impacted fractionated coal fly ash: Implications for CO₂ sequestration. *J Environ Manag* 92: 655-664.
44. O'Connor WK, Dahlin DC, Nilsen DN, Rush GE, Walters RP, et al. (2001) Carbondioxide sequestration by direct mineral carbonation: Results from recent studies and current status. Albany, Oregon, USA: Albany Research Center.
45. Ophardt CE (2003) Temperature and Pressure effect on solubility. *Virtual Chem Book*: Elmhurst college.
46. Page AL, Elsiwee AA (1979) Physical and chemical properties of fly ash from coal fired power plants with reference to environmental impacts. *Residue Rev* 71: 83-120.
47. Palumbo AV, Tarver JR, Fagan LA, McNeilly MS, Ruther R, et al. (2005) Potential for metal leaching and toxicity from fly ash applied for increasing carbon sequestration in soil. *World of coal fly ash* Lexington, Kentucky, USA.
48. Perera MSA, Ranjith PG, Airey DW, Choi SK (2011) Sub- and super-critical carbon dioxide flow behavior in naturally fractured black coal: An experimental study. *Fuel* 90: 3390-3397.
49. Polettini A, Pomi R (2004) The leaching behaviour of incineration bottom ash as affected by accelerated aging. *J Hazard Mater* 113: 209-215.
50. Rai UN, Pandey K, Sinha S, Singh A, Saxena R, et al. (2004) Revegetating fly ash landfills with *Prosopis juliflora* L: impact of different amendments and Rhizobium inoculation. *Environ Int* 30: 293-300.
51. Ram LC, Masto RE (2009) An appraisal of the potential use of fly ash for reclaiming coal mine spoil. *J Environ Manag* 91: 603-617.
52. Reddy KJ, Drever JI, Hasfurther VR (1991) Effects of a carbon dioxide pressure process on the solubilities of major and trace elements in oil shale solid wastes. *Environ Sci Technol* 25: 1466-1469.
53. Reddy KJ, Weber H, Bhattacharyya P, Argyle M, Taylor D, et al. (2010) Instantaneous capture and mineralization of flue gas carbon dioxide: pilot scale study. *Nature Precedings*.
54. Rendek E, Ducom G, Germain P (2006) Carbon dioxide sequestration in municipal solid waste incinerator (MSWI) bottom ash. *J Hazard Mater* 128: 73-79.
55. Riehl A, Elsass F, Duplay J, Huber F, Trautmann M (2010) Changes in soil properties in a fluvisol (calcaric) amended with coal fly ash. *Geoderma* 155: 67-74.
56. Sale LY, Chanasyk DS, Naeth MA (1996) Temporal influence of fly ash on soil bulk density and aggregate size distribution. 20th Annual British Columbia Mine Reclamation Symposium, 184-195 Kamloops, BC.
57. Sale LY, Chanasyk DS, Naeth MA (1997) Temporal influence of fly ash on select soil physical properties. *Can J Soil Sci* 77: 677-683.
58. Sarkar A, Rano R (2007) Water holding capacities of fly ashes: effect of size fractionation. *Energy Sourc Recovery Utilisa Environ Effects* 29: 471-482.
59. Sharma S, Fulekar MH, Jayalakshmi CP, Straub CP (1989) Fly ash dynamics in soil water systems. *Crit Rev Environ Control* 19: 251-275.
60. Sharma SK, Kalra N (2006) Effect of fly ash incorporation on soil properties and productivity of crops : A review. *J Sci Ind Res* 65: 383-390.
61. Shrestha RK, Lal R (2006) Ecosystem carbon budgeting and soil carbon sequestration in reclaimed mine soil. *Environ Int* 32: 781-796.
62. Shukla R, Ranjith P, Haque A, Choi X (2010) A review of studies on CO₂ sequestration and caprock integrity. *Fuel* 89: 2651-2664.
63. Sikka R, Kansal BD (1994) Characterization of thermal power-plant fly ash for agronomic purposes and identify pollution hazzards. *Biores Technol* 50: 269-273.
64. Sipilä J, Tei, S, Zevenhoven R (2008) Carbon dioxide sequestration by mineral carbonation: literature review: Faculty of Technology, Abo Akademi University Espoo, Finland.
65. Soong Y, Fauth DL, Howard BH, Jones JR, Harrison DK, et al. (2006) CO₂ sequestration with brine solution and fly ashes. *Energy Convers Manag* 47: 1676-1685.
66. Stolaroff JK, Lowry GV, Keith DV (2005) Using CaO and MgO- rich industrial waste streams for carbon sequestration. *Energy Convers Manag* 46: 687-699.
67. Tripathy A, Sahu RK (1997) Effect of coal fly ash on growth and yield of wheat. *J Environ Bio* 18: 131-135.
68. Tsadilas CD, Samaras V, Kazai P, Sgouras J (2002) Influence of fly ash and sewage sludge application on wheat biomass production, nutrients availability and soil properties. *Int J Coal Sci Technol* 1: 221-6.
69. Udeigwe TK, Eze PN, Teboh JM, Stietiya MH (2011). Application, chemistry, and environmental implications of contaminant-immobilization amendments on agricultural soil and water quality. *Environ Int* 37: 258-267.
70. Ussiri DAN, Lal R (2005) Carbon sequestration in reclaimed minesoils. *Plant Sci* 24: 151-165.
71. Van Gerven T, Van keer E, Arickx S, Jaspers M, Wauters G, et al. (2005) Carbonation of MSWI bottom ash to decrease heavy metal leaching, in view of recycling. *Waste Manag* 25: 291-300.
72. Wang L, Jin Y, Nie Y (2010) Investigation of accelerated and natural carbonation of MSWI fly ash with a high content of Ca. *J Hazard Mater* 174: 334-343.
73. Wong JWC, Wongz MH (1987) Co-Recycling of fly ash and poultry manure in nutrient-deficient sandy soil. *Resour Conser* 13: 291-304.
74. Yan J, Bäverman C, Moreno L, Neretnieks I (1997) The long-term acid neutralizing capacity of steel slag. *Stud Environ Sci* 71: 631-640.