

CO₂ SEQUESTRATION THROUGH MINERAL CARBONATION OF FLY ASH AND ITS USE IN AGRICULTURE

S.D. Muduli*, B.D. Nayak and N.K. Dhal

Institute of Minerals and Materials Technology, Bhubaneswar

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ABSTRACT:

Emission of CO₂ from different sources has increased the effect of green house gases and global warming. Fixation of CO₂ from atmosphere in the form of solid carbonates appears to be an option for reduction of CO₂ concentration. Mineral carbonation is a process of chemical reaction in which minerals or its residues consisting of lime and magnesia become a source of carbonation. The material fly ash and gypsum are industrial wastes and causes disposal problem leading to environmental pollution. Gypsum (bassanite) is a calcium bearing material and fly ash contains silica and alumina. Combination of these materials provides a favorable ingredient for mineral carbonation. The combination of fly ash and gypsum in long term storage under atmospheric condition becomes a site for capturing atmospheric CO₂. The bulk use of this carbonated ash was carried out in agricultural purpose to explore the feasibility of utilizing fly ash in improving the productivity of an acid lateritic soil through pot culture study. With this concept field experiments had conducted in medicinal plant garden site in two fast growing tree species i.e. *Acacia mangium* and *Dalbergia sisso* in carbonated ash with different concentration. Taking various parameters like PH, EC, and WHC into consideration, the periodical growth rate of *Acacia mangium* showed better response. The present paper will highlight the growth performance and sustainable use of fly ash in agriculture.

1. INTRODUCTION

In recent years the amount of CO₂ in the atmosphere has increased significantly and rapidly reaching 384 ppm in 2007 (Lackner et al., 1995). The steep increase in atmospheric CO₂ concentration is alarming and it has been attributed as a major factor in the increase of earth's temperature. More than 7 Gtons of anthropogenic CO₂ are released to the atmosphere including a major contribution from the production of steel by the steel works each year (Liu et al., 2000). The CO₂ causes about 6-29% of the green house effect on the earth (Kiehl et al., 2006), as a result it helps in global warming and climate change. To minimize CO₂ emission mineral carbonation is a process by which carbon dioxide is absorbed from the atmosphere and stored indefinitely. Mineral carbonation is an interesting concept which involves permanent storage of CO₂ in silicate materials and alkaline solid materials as carbonate minerals. Alkaline solid materials are naturally carbonated by absorbing atmospheric CO₂ because these solids contain a variety of thermodynamically unstable oxides, hydroxides, and silicate materials that can capture and convert CO₂ into carbonates. Till date the majority of mineral carbonation research has examined in mined silicate minerals (Lackner et al., 1995; Connor et al., 2002). The oxide mineral sources are readily available through the reuse of industrial solid wastes and residues. The end product of sequestration may be amendable for beneficial re-use in construction material, agricultural etc.

The thermal power plant industries produce millions tons of coal fly ash each year which consists of fine particles of unburnt raw materials and some trace elements. Although a fraction of this is used for beneficial agricultural application, the industries dispose off several million tones annually in piles, quarries and landfills.

Earlier workers have expressed increased concern over environmental pollution associated with the improper management of fly ash and gypsum. Therefore waste neutralization through sequestration may be an encouraging means to both capture carbon and mitigate the possible adverse health and environmental effects posed by improper disposal of fly ash and gypsum. Fly ash has a vast potential for use in agriculture as an amendment especially due to its physical condition which are conducive for plant growth as well as due to the presence of macro and micro nutrients in it. Soil properties as influenced by fly application have been studied by several workers (Aitken et al., 1984). Fly ash, which can be acidic or alkaline depending on the source, can be used to buffer the soil pH (Phung et al., 1978). Application of fly ash for increasing the pH of acidic soils (Phung et al., 1979) and improving soil texture (Chang et al., 1977) was investigated for agronomic benefits (Plank et al., 1975; Adriano et al., 1980;) and improving the nutrient status of soil (Schnappinger et al., 1975; Rautaray et al., 2003). Agricultural utilization of fly ash has been proposed because of its considerable content of K, Ca, Mg, S and P (Page et al., 1979; Adriano et al., 1980; Singh et al., 1997). Fly ash addition generally increases plant growth and nutrient uptake (Aitken et al., 1984).

Researchers all over the world are searching new plant species suitable to be used in phytoremediation. While selecting a species for phytoremediation several factors have to be taken into account. The species should be fast growing, high biomass producing, with Profuse root system, tolerant to adverse environment condition, and non edible and economically beneficial (Alkorta, et al., 2004). With this concept two fast growing tree species i.e. *Acacia mangium* and *Dalbergia sisso* had been selected for pot culture study.

* surabhidipali@gmail.com

This paper represents the study of the feasibility of CO₂ capture through fly ash and gypsum mixture and identifies the conditions that appear to improve the extent of sequestration. Here authors have observed the feasibility of utilizing this carbonated fly ash in improving the productivity of an acid lateritic soil through pot culture study

2. MATERIALS AND METHOD

Fly ash collected from Power Plants and the gypsum (Bassanite) brought from Phosphate producing industries were used as experimental raw material. The chemical compositions of both the raw materials were shown in the table 1. Carbonated ash was prepared by mixing fly ash and gypsum with the help of an alkali activator in wet condition. The mineralogical composition of the raw material was determined by X-ray diffraction. Three types of substrates were chosen to observe the feasibility of plant growth during the experiment; (i) garden soil serving as control (G); (ii) 100% fly ash (O); and (iii) mixture of activated fly ash and garden soil (M) in the ratio of 3:1 (Table 2). Fly ash collected from Power Plants and the gypsum (Bassanite) brought from Phosphate producing industries were used as experimental raw material. Experiment was set up inside the green house, in pots. Replicates were taken per treatment. The *Acacia mangium* and *Dalbergia sisso* seedling were planted in the pot. The plants were allowed to grow in green house and watered at regular intervals to keep the soil saturated. After 180 days of transplantation, the plants were studied for the changes in growth.

Major Elements	Fly ash (wt %)	Gypsum (wt %)
SiO ₂	59.03	-
Al ₂ O ₃	25.86	0.5
Fe ₂ O ₃	5.81	0.55
TiO ₂	1.71	-
CaO	1.07	32.5
MgO	0.68	-
K ₂ O	1.89	-
Na ₂ O	0.07	-
P ₂ O ₅	0.72	0.45
SO ₄	-	54.6
F ₂	-	0.25

Table 1: Chemical Composition of Raw Material

Substrate	pH	Conductivity (µs/cm)	Water Holding Capacity (%)
Garden soil (G)	5.0	97	56
Fly ash (O)	6.9	108	66
Activated ash (M)	7.7	118	67

Table 2: Physical characteristics of substrate

3. RESULTS AND DISCUSSION

3.1 Different Growth Parameters of Plants

Analysis of X-ray diffraction of the mixture of fly ash Gypsum, water and chemical booster after 30 days of atmospheric exposure shows intermediate reaction phases such as Scawtite, and Calcite. The samples examined by DTA/TG indicate a major weight loss at 165° C and 710° C. The weight loss at 165° C is due to the loss of structural water creating an intermediate phase like Scawtite. The loss at 710° C is due to the decomposition of Carbonate phase that forms in the reaction process. The X-ray Diffraction and DTA/TG analysis shows that there is appreciable formation of carbonate phases. Here from the experiment it is observed that calcium carbonate has detected in significant amount which is a single form of calcite in the carbonated fly ash gypsum mixture. Carbonation of fly ash begins by addition of CaSO₄ to the mixture that is followed by the diffusion of calcium from gypsum which develops an alkaline condition and promotes in dissolution of silica and alumina of fly ash. In the process of dissolution, fly ash reacts with gypsum to form many hydrous intermediate unstable phases. By subsequent interaction and absorption of CO₂ from atmosphere these unstable intermediate phases breaks to stable carbonate structures which converted the fly ash into a clay structure. Our study showed that although the fast growing tree species survived 100% in all three substrates, but activated ash showed the better growth response. Activated ash is relatively alkaline than fly ash followed by garden soil. Water holding capacity of activated ash is comparatively better than other two substrates. From the field experiment it was observed that growth response of *Acacia mangium* and *Dalbergia sisso* seedling through activated ash was better (Table 3), which indicates mineral carbonation of fly ash can absorb atmospheric carbon dioxide and be reutilized in agriculture under waste management programme creating ample scope for further study.

Name of Plant	Type of Treatment	During Seedling		After 180 Days	
		Height (cm)	Girth (cm)	Height (cm)	Girth (cm)
A. mangium	Garden soil (G)	35	2	41	3
	Fly ash (O)	33	2	43	4
	Activated ash (M)	30	2	157	6
D. Sisso	Garden soil (G)	36	2	46	3
	Fly ash(O)	30	2	53	4
	Activated ash (M)	38	2	78	6

Table 3: Growth Response of *Acacia Mangium* and *Dalbergia Sisso* Under Three Different Treatments

CONCLUSION

The present study reveals that the chemical composition of fly ash and gypsum create a suitable condition for atmospheric CO₂ sequestration. In this process hydration mechanisms are involved through intermediate unstable phases. The main hydration product detected in the mixture is calcite and Scawtite. The incorporation of fly ash and gypsum mixture through mineral carbonation contribute as a good substrate for agriculture. Mineral carbonation of fly ash for carbon dioxide sequestration and its use in agriculture is a better option for sustainable environment and waste management.

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REFERENCES

- Lackner, K.S., Wendt, C.H., Butt, D.P., Joyce, E.L., Sharp, D.H., 1995, Carbon dioxide disposal in carbonate minerals, *Energy*, (20), pp. 1153–1170.
- Liu, Z.: Zhao, J., 2000, *Contribution of carbonate rock weathering to the atmospheric CO₂ sink*. *Environ. Geol.* 39, 1053.
- Kiehl JT, Kevin E. Trenberth., 1997 Earth's annual global mean energy budget (PDF). *Bulletin of the American meteorological society* 78(2): 197-208. Doi: 10.1175/1520-0477(1997)078<0197:EAGMEB>2.0.CO;2 [Retrieved on 1 may 2006].
- W.K. O Connor, D.C. Dahlin, G.E. Rush, CL. Dahlin, W.K. Collins., 2002 Carbon dioxide sequestration by direct mineral carbonation: Process mineralogy of feed and products, *Minerals & Metallurgical processing* 19 (2) pp. 95–101.
- Aitken, R.L., Campbell, D.J., Bell, L.C., 1984. Properties of Australian fly ash relevant to their agronomic utilization. *Aust. J. Soil Res.* 22, pp. 443–453.
- Phung, H.T., Lund, L.J., Page, A.L., 1978. Potential use of fly ash as a liming material. In: Adriano, D.C., Brisbin, I.L. (Eds.), *Environmental Chemistry and Cycling Processes*, CONF-760429. US Department of Commerce, Springfield, VA, pp. 504–515.
- Phung, H.T., Lam, H.V., Lund, L.J., Page, A.L., 1979. The practice of leaching Boron and salts from fly ash amended soils. *Water, Air Soil Pollut.* 12, 247–254.
- Chang, A.C., Lund, L.J., Page, A.L., Warneke, J.E., 1977. Physical properties of fly ash amended soils. *J. Environ. Qual.* 6 (3), pp. 267–270.
- Plank, C.O., Martens, D.C., Hallock, D.L., 1975. Effect of soil application of fly ash on chemical composition and yield of corn (*Zea mays* L.) and on chemical composition of displaced soil solutions. *Plant Soil* 42, pp. 465–476.
- Adriano, D.C., Page, A.L., Elseewi, A.A., Chang, A.C., Straughan, I., 1980. Utilization and disposal of fly ash and other coal residues in terrestrial ecosystems: a review. *J. Environ. Qual.* 9, pp. 333–344.
- Schnappinger Jr., M.G, Martens, D.C., Plank, C.O., 1975. Zinc availability as influenced by application of fly ash to soil. *Environ. Sci. Technol.* 9, pp. 258–261.
- Rautaray, S.K., Ghosh, B.C., Mitra, B.N., 2003. Effect of fly ash, organic wastes and chemical fertilizers on yield, nutrient uptake, heavy metal content and residual fertility in a rice-mustard cropping sequence under acid lateritic soils. *Bioresour. Technol.* 90, pp. 275–283.
- Page, A.L., Elseewi, A.A., Straughan, I.R., 1979. Physical and chemical properties of fly ash from coal-fired power plants with special reference to environmental impacts. *Residue Rev.* 71, pp. 83–120.
- Singh, S.N., Kulshreshtha, K., Ahmad, K.J., 1997. Impact of fly ash soil amendment on seed germination, seedling growth and metal composition of *Vicia faba* L. *Ecological Eng.* 9, pp. 203–208.
- Aitken, R.L., Campbell, D.J., Bell, L.C., 1984. Properties of Australian fly ash relevant to their agronomic utilization. *Aust. J. Soil Res.* 22, pp. 443–453.
- I. Alkorta, J. Hernández-Allica, J.M. Becerril, I. Amezaga, I. Albizu, C. Garbisu, Recent findings on the phytoremediation of soils contaminated with environmentally toxic heavy metals and metalloids such as zinc, cadmium, lead, and arsenic, *Rev. Environ. Sci. Biotechnol.* 3 pp. (2004) 71–90.