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Capture of carbon dioxide emitted from coal fired thermal power station using fly ash slurry

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Abstract: In India, coal is the major fossil fuel used in power plants for power generation. The carbon dioxide emitted as a product of combustion of coal (fossil fuels) is responsible for change in climatic conditions globally. Hence, capture of carbon dioxide emitted from coal fired thermal power station using ash slurry, which is let out as waste stream from thermal power station has been explored under saline conditions at normal atmospheric pressure without adding any chemical reagents/solvents. Work was carried out by varying pH of the slurry and ratio of bottom ash to fly ash mixture as slurry. The result shows that the percentage of CO_2 reduction increases with increase in pH. A maximum of 90% reduction was achieved with slurry pH of 9.3. It was also found that ratio of (3:1) bottom ash to Fly ash slurry is best suited for reduction of CO_2.
Keyword: Fly ash, Brine, CO_2.

Introduction

CO_2 emission is of great concern in view of its impact on global warming. Thermal power plants emits greenhouse gases (GHGs), carbon dioxide (CO_2), sulphur oxides (SO_x), CFCs and nitrogen oxides (NO_x) due to combustion of coal. Other trace gases and air borne inorganic particulates, such as fly ash and suspended particulate matter (SPM) are also generated. Due to the combustion of fossil fuels and deforestation, Carbon dioxide percentage has increased by about 25%. It has been reported that the average concentration of CO_2 in the atmosphere has already reached358 ppm by volume (ppmv), compared to the pre-industrial level of 280 ppmv. It is estimated that CO_2 emissions into the atmosphere will increase the earth's surface temperature by approximately 1.5–4ºC in the next 30–40 years[1]. The International Energy Agency in World Energy Outlook 2000 has also reported that the global CO_2 emissions would increase to 36,102 million tonnes in 2020[2]. In most developing countries, CO_2 emissions are between 0.3 and 0.6 tons of carbon per capita per year. The fossil fuels share in energy generation, along with their CO_2 emission, is presented in Table 1.[3]. Hence CO_2 capture from coal fired power station is to be prioritized to reduce the effect of global warming.

Table 1. Fossil fuels share

Fuel	Energy generation (%)		Carbon emission (%)	
	India	World	India	World
Coal	55	20.3	69.78	41.2
Oil	30.5	41.3	26.31	42.65
Natural gas	7.0	21.1	3.9	16.12

CO_2 capture and storage (CCS) processes are proposed[4,5]. The CO_2 capture technologies include membrane separation technologies, sorbent technologies involving pressure or temperature swing processes, and the use of solvents such as mono ethanolamine[6,7]. The CO_2 storage processes include subsurface pressure injection into geologic strata and reservoirs of saline, oil, and gas[8]. Mineral carbonation using different industrial residues like coal fly ash/bottom ash, municipal solid waste (MSW) has been reported elsewhere[9-14] .Objective of this study is to evaluate the application of brine impacted fly ash a waste stream generated in thermal power plant for the mitigation of gaseous carbon dioxide emitted from the same thermal power plant.

Materials and Methods

Ash Slurry & Flue Gas

In this work, fly ash slurry and direct flue gas generated from 'North Chennai thermal power station' (NCTPS), were used to capture CO_2. This power plant is located at North Chennai near Ennore creek with installed capacity of 3 X 210 MW Coal fired Thermal power station. The compositions of Flue gas, sea water and Fly ash are given in tables (2-4).In this thermal power stations about 20 % of ash is collected as bottom ash from hopper after quenching the combusted coal using sea water and then passed through clinker grinder for grinding into finer particles and the final form of slurry is let out for further deposal .Similarly about 80 % ash collected from Electro Static Precipitator (ESP) is evacuated Pneumatically and stored in the Fly ash hopper for sale and the balance 20 % is mixed with sea water in the mixing apparatus at the bottom of the ESP hoppers and is let out as slurry .

Fly Ash is classified as Class F as per ASTM C 618. Class F fly ash has lime (CaO) content <10%. Fly ash particles are very fine, light weight (density 1.97–2.89 g/cc) and have spherical shape (specific surface area 4000–10,000 cm^2/g; diameter of 1–150 μm).

Table: 2 Flue gas compositions:

CO_2	CO	NOx	SOx ppm	SPM mg/NM^3
15%	Nil	93	105	100

Table: 3. Sea water analysis

Conductivity Microsieman/cm	pH	TDS ppm	Ca ppm	Mg ppm	Silica ppm
55500	8.5	32640	1360	4400	0.32

Table: 4. Fly ash composition

SiO_2	Al_2O_3	Fe_2O_3	Ca	Mg
57.60 %	29.5 %	6.6 %	1.5 %	0.5 %

Methodology

A column made up of plexi glass of 1 m length and 100mm diameter with an inlet and out let arrangements for flue gas was used. Flue gas bladders were connected to the inlet and outlet of the column. Initially a known quantity of ash slurry was taken in the column. Then flue gas from the bladder was passed through the column at a flow rate of 6.6 g/min. Initial and final pH of the slurry was measured. Flue gas sample collected after bubbling through column was tested for %CO_2removal using ORSAT apparatus. The effect of ash slurry pH and ash slurry (Bottom ash and Fly ash) ratio mixture on CO_2 Capture (CC) was studied.

Reactions

The chemical reactions involved in CC by using ash slurry column are listed below

i) Physical absorption of CO_2 by the Ash Slurry under saline condition
ii) Leaching of minerals in ash slurry under Alkaline condition leads to the formation of its Carbonates by mineral carbonate when reacts with CO_2 [15]

$$CO_2 + H_2O \Leftrightarrow H_2CO_3$$
$$H_2CO_3 \Leftrightarrow H^+ + HCO^{3-}$$
$$HCO^{3-} \Leftrightarrow H^+ + CO^{3-}$$
$$CaO + H_2O \rightarrow Ca(OH)_2$$
$$Ca(OH)_2 \rightarrow Ca^{2+} + OH^-$$
$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$$

iii. Coal combustion fly ash contains oxides such as CaO and MgO that can be converted to carbonates in the presence of CO_2 through the above sequence of reactions.

i) Solubility of CO_2 in Sea water forms Carbonic acid
ii) Solubility of CO_2 in Sea water forms Carbonic acid

$$CO_2 + H_2O \rightarrow H_2CO_3$$

Results and Discussion

Effect of Ash Slurry Composition

The effect of, different ratios of ash slurry (Bottom ash and Fly ash) on removal is shown in Figure.1 It can be observed from plot that Normal Slurry (BA 20 % + FA 10 %) ratio of bottom ash to fly ash mixture showed maximum CO_2 reduction compared to other ratios of fly ash This may be due to the solid content present in that ratio as shown in table 5. However the effect of ash slurry do not have appreciable effect on absorption.

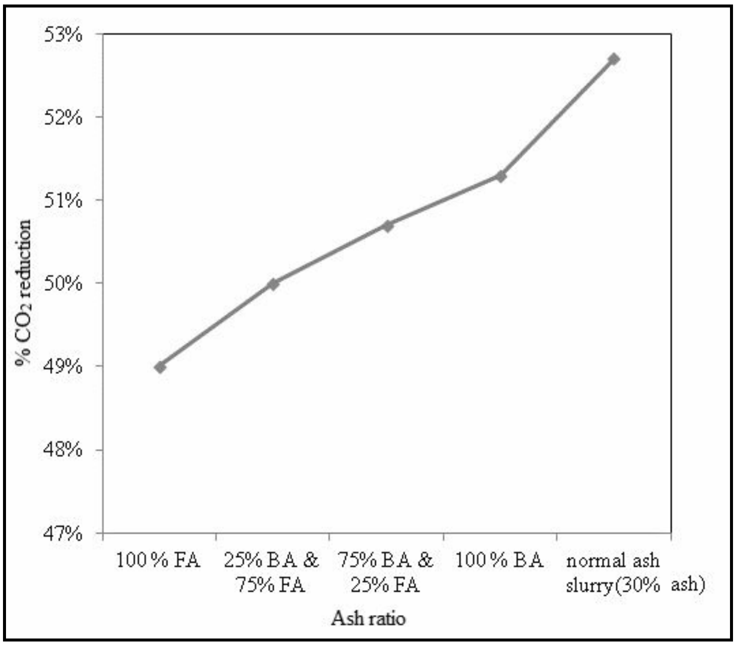

Fig.1. Effect of ash ratio on CO_2 removal

Table 5. Different ratios of ash slurry (Bottom ash to Fly ash)

Ash combination	Ash (solid content)	Water (Liquid content)
25% BA(Bottom Ash) & 75% FA(Fly Ash)	12.5	87.5
75% BA & 25% FA	17.5	82.5
100 % BA	20	80
100 % FA	10	90
Normal Slurry(BA (20 %) + FA (10 %))	30	70

Effect of pH On CO_2 Reduction

Effect of pH on CO_2 removal is shown in Figure.2 It can be observed from figure that the CO_2 removal increases with increase in pH showing 90% removal. It has been reported that alkaline slurry will have more CC [16]

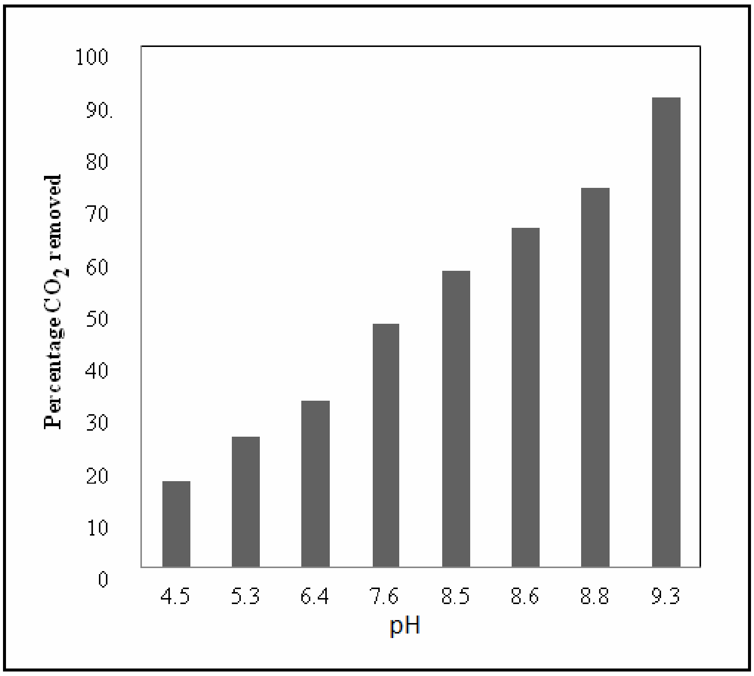

Fig.2. Effect of pH on CO_2 removal.

Characterisation using SEM

Scanning Electron Microscopy (SEM) Images were used to determine the texture and composition of the fly ash slurry at its fresh stage (before) and after absorption of CO_2. The Scanning Electron Microscopy (SEM) images was analyzed by the TESCAN VEGA3 SBU VG8251177IN (Czech Republic). Figure 3(a-b) shows SEM images of uncarbonated fly ash slurry before the start of the operation. Figure 3(a) and (b) of fresh uncarbonated fly ash shows the presence of spherical particles containing cenospheres and plerospheres formed as a by-product of coal combustion process. Figure.3 (c-d) are those of carbonated fly ash slurry (i.e after absorption of CO_2). SEM Images obtained after CO_2 absorption showed a change in the spherical structure of cenospheres and plerospheres. Formation of cubic and rod shaped crystallite structures were seen. The transformation from spherical to "cube-like" structure can be attributed to the formation of a secondary phase of calcite particles on to the surface of ash. The presence of "rod-shaped" structures is due to the formation of aragonite on the fly ash surface and the coaly fragments of fly ash are found to be rich in minerals. Hence an increase in the carbon content after the absorption process can be attributed to the formation of amorphous or crystallite carbonate materials on the fly ash surface.

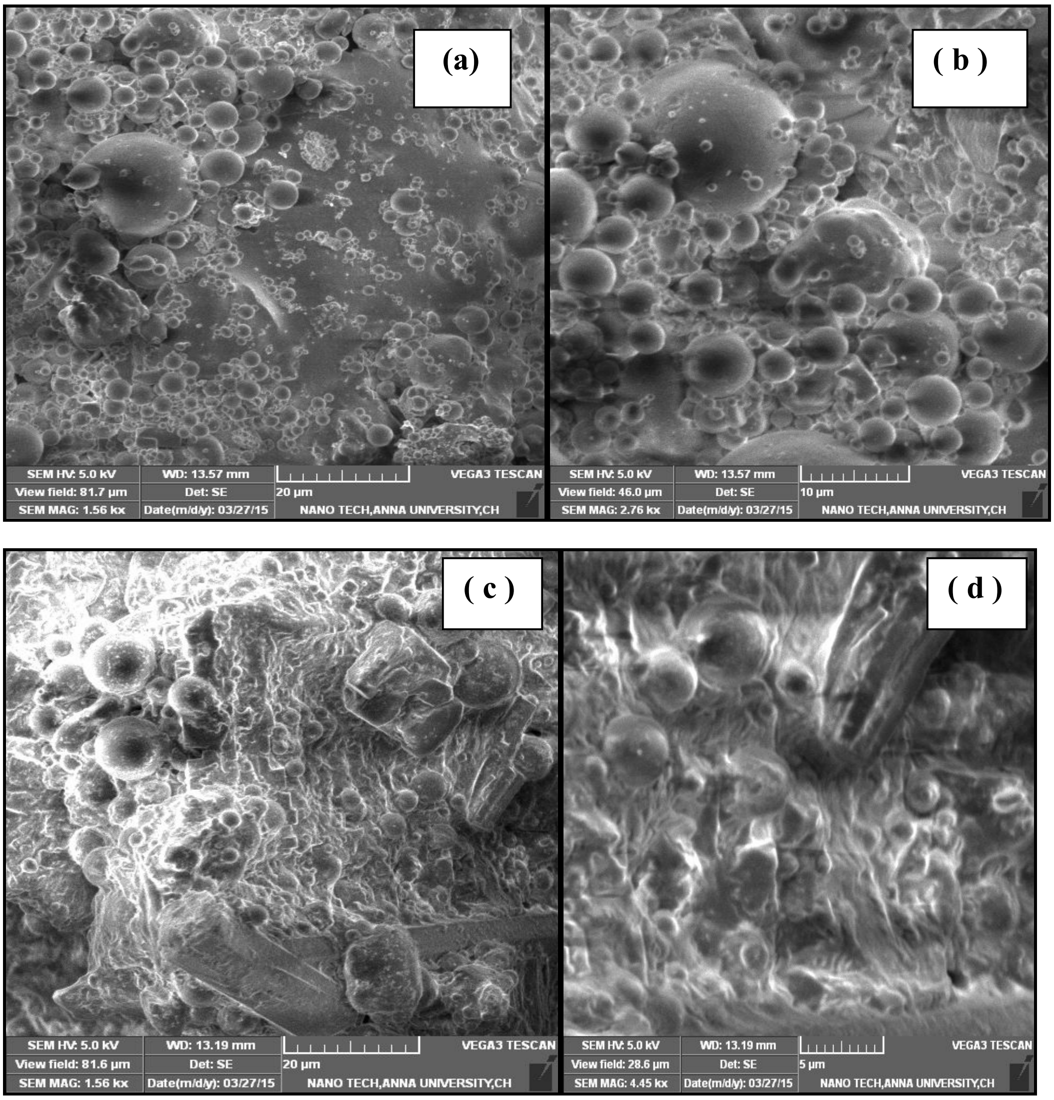

Fig 3. SEM Images of (a-b) Uncarbonated and (c-d) Carbonated fly ash slurry

Characterization using XRD

X-Ray Diffraction Analysis is one of the most important non- destructive tools to analyse all kinds of matter ranging from fluids to powders and crystals. A diffractogram is obtained from the analysis which is a graph of diffracted intensity as a function of scattering angle, 2ϴ. Identification of unknown materials is done by the comparison of the diffractogram peaks with known standards. XRD data was obtained using the XRD spectrum data analyzer Xpert-Pro-PAN Analytical Instrument using the CUKα radiation with 30(mA) and 45(kV).

Figure 4 shows the XRD Spectrum of fly ash before treatment and after absorption of CO_2. In the fresh fly ash before treatment, peaks were obtained at 2ϴ values of 16.39, 20.81, 25.93, 26.21, 26.57, 31.65, 35.18, 40.75, 50.01, 56.38 and 57.48. The peaks depicted by 2ϴ angle of 16.39, 25.93, 26.21, 26.57, 35.18 and 60.59 show the presence of mullite in the fly ash. Peaks obtained at 2ϴ of 20.81 and 50.01 are due to the presence of Quartz in the fly ash. Small peaks obtained at 40.75, 56.38 and 57.48 are due to the presence of hematite in the sample and a peak at 31.65 is due to magnetite present.

In the carbonated fly ash obtained after treatment distinct peaks were observed at 2ϴ values of 32.10, 45.80, 45.87, 56.77, 65.58, 75.52 and 84.28. A sharp peak obtained at 32.10 is due to the presence of calcite present in the sample, peaks at 45.80 and 45.87 is due to the presence of plagioclase present in the carbonated fly ash. Peaks at 56.77, 66.58 and 84.28 is due to hematite, peaks at 66.58 and 75.52 are due to the presence of quartz. Hence it can be seen that the dominant peaks of mullite showed in the fresh fly ash samples disappeared and calcite was found to be predominantly present in the carbonated sample.

Estimation of CC using Ash Slurry of Varying PH

The quantity of flue gas generated in a thermal power station is estimated based on the stoichiometric equations involved in the combustion of coal. This will vary according to the chemical composition of Coal (ultimate analysis) and quantity of coal & air supplied to the boiler furnace. The estimated values are given in Table 6.

Table 6. Estimated flue gas and CO_2

Properties	**Indian coal**	**Imported coal**	**Blended Coal (78 % Indian and 22 % Import)**	
Moisture	6.30	9.40	6.98	**Ultimate analysis of Coal**
Ash	46.80	12.50	39.25	
Carbon	32.94	59.78	38.86	
Hydrogen	2.21	4.36	2.68	
Nitrogen	1.67	1.33	1.59	
Sulphur	0.41	0.56	0.44	
Oxygen	9.67	12.07	10.20	
Total (Kg)	100	100	100	
Calorific Value (kCal/kg)	3086	5096	3528.2	
Specific Fuel consumption with Heat rate of 2494 kCal/kWh	0.81	0.49	0.71	
Total Air required with excess air	538	984.36	635.67	
Flue gas quantity(kg) generated for complete combustion of 100 Kg of Coal	679.6	1244.11	803.27	
Coal consumption (T/h) for 210 MW Generation	170.1	102.9	149.1	
Flue gas flow for 210 MW power generation (T/h)	1156	1280.19	1197.68	
Qty. Of CO_2 @ 15 % in the Flue gas (T/h)	173.4	192.03	179.65	
Qty. Of CO_2 @ 7.1 % in the Flue gas after bubbling in the ash slurry of pH 8.5 (T/h)	82.08	90.89	85.04	
Qty. Of CO_2 @ 1.5 % in the Flue gas after bubbling in the ash slurry of pH 9.3 (T/h)	17.34	19.2	17.97	
CO_2 Capture by the ash slurry of pH -8.5 (T/h)	91.32	101.14	94.61	
CO_2 Capture by the ash slurry of pH -9.3 (T/h)	156.06	172.83	161.68	

Estimation of Ash Slurry Quantity For CC From Flue Gas

About 20 % of bottom ash and 10 % of Fly are mixed with sea water at the solid and liquid ratio of 1: 25 for easy disposal by ash slurry pumps. The ash slurry generated in thermal power station is shown in the table 7. In addition to the sea water required for making the slurry, additional quantity of sea water is used for sealing the bottom hopper of boiler furnace and ESP hopper so as to avoid air ingress from atmosphere to the flue gas path, hence the total volumetric flow of slurry increases from 700 to 850 (m^3/h). This volumetric flow is available for CC.

Table 7. Estimated ash slurry quantity

Sl.No.	Description	Indian T/h	Imported T/h	Blended Coal with 78 % Indian and 22 % Import T/h
1	Coal consumption for 210 MW	170.1	102.9	149.1
2	Ash content of Coal (%)	46.8	12.5	39.25
3	Total Ash generation (T/h)	79.60	12.86	58.52
4	Bottom ash slurry (T/h)-20 %	15.92	2.57	11.70
5	Fly ash (T/h)-80 %	63.68	10.29	46.82
6	Fly ash slurry (10 %)	6.37	1.03	4.68
7	Total ash slurry T/h	22.29	3.60	16.39
8	Sea water required (m^3/h)	557.25	90.04	409.70

Conclusion

Mitigation of CO_2 is essential to reduce the effect of global warming and the method for CC from flue gas using ash slurry, a waste stream from thermal power stations that is having more potential to absorb CO_2, is cost effective and a reliable process in CO_2 reduction. This method does not require any chemical reagents or any pressurized reactors or heating /cooling process as required for currently available methods for CC.

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