Feasibility Analysis of Coal Combustion Residues as Fertilizer for Agricultural Use

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Abstract
Coal combustion residues are generated in huge amount by more than 120 existing thermal power stations in India. Disposal of fly ash is a great challenge before the thermal power station management. Coal combustion residues can be a good option and can be widely used in agriculture applications in bulk. In the present work a study on macro-nutrients and bio-available micro-nutrients has been carried out. The aim of the study is to assess the suitability of coal combustion residues as fertilizer for agriculture use. Such use will definitely help in utilizing the waste as a resource material in bulk and will also be useful in reducing the environmental impact of coal combustion residues generation to some extent. The methodology of the study includes the determination of available NPK and bio-available (DTPA) extractable elements such as Fe, Cu, Mn, Zn, Pb, Ni, Cr, Cd, and Co. The nutrient status of the coal combustion residue was determined using DTPA extraction method. Available Nitrogen (N) was determined by the Kjeldhal extraction and titration technique, available phosphorous (P) by Olsen's method and available potassium (K) by ammonium acetate method. From the experimental study it was found that coal combustion residue under study is a good source of NPK and bio-available (DTPA) extractable elements and as such it has the potential for use in agricultural sector. Abandoned surface mines devoid of necessary nutrients can be revegetated using coal combustion residues.

This study covers parameters like pH, electrical conductivity, CCE, Organic Carbon, and $CaCO_3$ (%). Ultimate analysis was performed using the standard procedures to determine the elemental composition in terms of C, H, N, S and O. Besides, XRD study was also carried out. All this was done to provide the basic scientific data for CCR utilization in varied fields.

Keywords: Macro-nutrients, micro-nutrients, thermal power station, agriculture applications, coal combustion residues.

Introduction

Coal combustion residues (CCRs) that have been considered a waste material in the past and were usually disposed of in wet form in an impoundment especially made for this purpose have posed numerous ecological and environmental problems. However, recent researches have shown that fly ash has potential to act as an invaluable ingredient in cement and concrete if used within the framework of prescribed specifications and quality systems. The fly ash is now considered as a resource material rather than a waste in civil engineering and material science.

In addition, fly ash can be gainfully used for various other applications including soil reclamation, mine fill material, stowing material etc. owing to its several characteristics that it possess. CCRs offer itself a good option and can be widely used in agricultural applications in bulk. It can be used in a number of beneficial ways like improving soil physical conditions, e.g. water infiltration, soil water holding capacity, hydraulic conductivity, bulk density and soil aggregation aggregation[1,16,17].

It can also help alleviate soil compaction and improve aggregate stability of sodic soils[6]; can supplement useful plant nutrients e.g. P, Ca, S, and Mg, K, Fe, Mn, Zn, Cu, and B[12] and can help correct acidic pH conditions[3,14,15].

Although soils bear the capacity of supporting vegetation, there are areas where soils have low pH and also have low contents of calcium and other nutrients. For such areas CCRs can be a good option for improving soil fertility status. Besides, soils water holding capacity can be greatly improved by the addition of suitable CCR materials. However, CCR application must be appropriately designed keeping in mind the achievable characteristics, CCR characteristics and the site characteristics where desired to be used.

The disposal of such large quantity of fly ash is indeed a challenge before all stakeholders. In this study an effort has been made to outline the present status of generation, utilization and future strategy to increase effective use of this wonderful material. The experimental study herein covers the feasibility analysis of CCR as fertilizer for agriculture use.

Literature survey revealed that several studies on wasteland reclamation agriculture applications of CCRs have been carried out as cited in table 1.

Study Area

The Fertilizer Corporation of India, Sindri was located at a distance of 26 kilometers from Dhanbad at latitude of 23°39' N and longitude 86°29' E just above the Tropic of Cancer and at an elevation 150m to 156m above mean sea level. The fertilizer unit was located on the bank of the river Damodar and was surrounded by the collieries of Bharat Coking Coal Ltd., the ACC Cement factory and Sindri Township.

Management has been taking every possible step to keep the pollution whether air or water under control. For this, several long and short-term measures were there for the control of pollution. As far as solid waste fly ash and bottom ash were concerned, these were collected in the hopper and below the incinerator respectively, made into the slurry form and via pipeline sent to the ash pond where it was stored for a longer period and was commonly referred as pond ash.

Samples: The pond ash samples from the steam generation plant of Fertilizer Corporation of India Ltd., Sindri were collected on five different days in a week and these were mixed in appropriate proportions to result in final homogenized samples. Pond ash samples were collected from four different ash ponds of different ages. The samples were labeled as S1, S2, S3 and S4.

Methodology: The nutrient status of the CCR was determined using DTPA extraction method. The trace elements and the heavy metals include Pb, Zn, Cu, Fe, Mn, Ni and Cd. In this DTPA is used. DTPA acts as chelating agent. The extraction was done at the pH of 7.3. The reagent used was DTPA (Diethylene Triamine Pentaacetic acid) extraction solution. The solution contains 0.005M DTPA, 0.01M $CaCl_2$ and 0.1M TEA adjusted to pH 7.3 with HCl. The extraction solution was prepared using 1.967g DTPA, 14.92g TEA and 1.47g $CaCl_2.2H_2O$ were added in approximately 200ml of double distilled water. Sufficient time was allowed to dissolve DTPA and then 800ml double distilled water was added to it. The pH was adjusted to 7.3 with dilute HCl while stirring. This solution thus made is stable for several months.

Available Nitrogen (N) was determined by the Kjeldhal extraction and titration technique, available phosphorous (P) by Olsen's method and available potassium (K) by ammonium acetate method. The elements were analyzed in flame photometer (Systronic Flame Photometer Model 128 for potassium measurement) and Atomic Absorption Spectrophotometer GBC-902 for analysis of other elements.

Other parameters like pH, electrical conductivity, CCE, Organic Carbon, % $CaCO_3$ were also studied. Ultimate analysis was performed using the standard procedures to determine the elemental composition in terms of C, H, N, S and O.

X-ray diffraction study was carried out using Philips X-ray Diffractometer (Philips PW 1011). X-ray diffraction (XRD)[11] is a versatile analytical technique used in research, production and quality control environments to identify crystalline materials. X-ray (powder) diffraction patterns of different fly ash samples were obtained with scanning speed of 1° per minute and the operating conditions involved the use of CuKα radiation at 34 KV 24 mA and Ni-filter. Various crystalline phases were identified by comparison with standard JCPDS (Joint Committee on Powder Diffraction Standards) files for inorganic compounds published by International Center for Diffraction Data, USA.

Results and Discussion

The CCR samples from Fertilizer Corporation of India, Sindri were analyzed for various chemical characteristics. The observation of the study is presented in table 2 and shown graphically in figure 1.

Table 1
Some studies on Wasteland Reclamation Agriculture Applications of CCRs

S.N.	Key Findings
1.	Certain variety of Indian beans can be successfully grown on the unamended fly ash. When mixed with soil in different proportion it can be used for growing food crops and pulses etc.[2]
2.	Vegetation can be grown on fly ash either alone or mixed with soil in different proportions.[10]
3.	Fly ash can be used as carrier in bio-fertilizer formulations which would be safe and effective alternatives to chemical fertilizers.[7]
4.	Study has established that the physical, chemical and biological properties of problematic soils can be improved for effective productivity of crops.[13]
5.	The study proves that fly ash can provide nutrients to support plants, can be used in amending acidic soils and wasteland. The study of lemon grass on fly ash ponds has established that it can be grown successfully without any amendment or treatment.[4]
6.	More than 20 mg/kg concentration of boron was observed in the fly ash. This proves that the fly ash can be used as soil amendment in boron deficient soils of Thailand.[5]
7.	The paper covers the beneficial as well as the negative effects of the use of fly ash in agriculture.[9]
8.	The study has shown that CCR contains micro nutrients as well as NPK elements and as such it has the potential use in the agriculture sector.[7]

The four samples were analyzed for pH, electrical conductivity (EC), organic carbon (OC), available NPK, cation exchange capacity (CEC), calcium carbonate ($CaCO_3$), ultimate analysis and DTPA extractable elements. Table 3 shows the fertility rating chart which is used to compare the experimental data with respect to the feasibility of the samples as fertilizer for agricultural use. Figure 2 shows the x-ray diffractograms for the four samples under study.

From the study it was observed that the pH of the samples varied from 6.0 to 7.2, electrical conductivity varied from 56 to 335 mS/cm, organic carbon varied from 0.610 to 1.349%, cation exchange capacity varied from 31.74 to 35.60 meq/100g and calcium carbonate varied from 1.0 to 1.5 %.

The four samples were also analysed for available nitrogen, available phosphorus, available potassium and DTPA extractable elements. Available nitrogen varied from 31.360 kg/ha in S4 to 87.810 in S2. Available P and available K ranged from 0.52 to 6.33 kg/ha and 170.24 to 358.40 kg/ha respectively, the maximum available P being in S4 and maximum available K being in S1. The value of the bio-available (DTPA) extractable Fe, Mn, Zn and Cu ranged from 6.642 to 9.626, 0.648 to 1.168, 1.358 to 2.750 and 0.734 to 1.724 ppm respectively. The presence of heavy metals as Pb, Ni and Co ranged from 0.102 to 0.164, 0.90 to 1.576 and BDL to 0.466 ppm respectively. Heavy metals as Cr and Cd were reported as BDL.

Results of the X-ray diffraction analysis are presented in table 4. The X-ray diffractograms are shown in figure 2. X-ray diffraction was performed to know the crystalline phases present in the CCR samples. From the results one can see that in all the four samples the major component consisted of quartz and the minor components included magnetite, hematite, pyrite and mullite. Pyrite was only observed in case of FCI S2 and mullite in case of all the FCI samples.

The observations of ultimate analysis in the form of CHNS are shown in table 2. Carbon content varied from 8.40 to 20.20%. Hydrogen varied from 0.32 to 0.61%. Nitrogen varied from 0.01 to 0.41%. Sulphur varied from 0.01 to 0.37%. Figure 3 shows the graphical representation of the CHNS study.

The pH of the four samples was found in the near neutral to neutral range. The minimum value was observed for S1 (6.07) and maximum was observed for S3 (7.21). This neutral nature of the CCRs can be used in amending both acidic and alkaline soils. Electrical conductivity indicates the different availability of ions in CCRs. The minimum value was observed for S2 (0.056) and maximum was observed for S1 (0.335). This high value of electrical conductivity for S1 CCR sample can well be compared with the open column leachate results where higher values were observed during the first flush phenomenon. The organic carbon of CCRs was between 0.23 to 1.896%. The maximum value was that of S4 and the minimum was that of S3 sample. On comparison with the fertility rating chart given below one finds that the CCRs had different fertility rating and as per the observations the samples S1, S2 and S4 had a high rating while S3 showed medium rating. In general, the samples exhibited higher organic matter.

The cation exchange capacity (CEC) of CCR samples was between 31.74 meq/100 g and 35.60 meq/100 g. The maximum value was that of S4 and minimum was that of S1. CEC of all the samples other than pond ash samples was above 30.00 meq/100g. In case of all the samples CEC was observed at higher value. Higher CEC requires a higher cations level to provide adequate crop rotation. Higher CEC also indicates that the materials have more buffering capacity and that more lime is needed to raise the pH by a specific amount. The calcium carbonate equivalent of CCRs was between 1 and 1.5%. Overall, CCE value was considerably less. Being neutral to alkaline in nature: CCRs can be used as an amendment material for acidic soils.

Pond ash characterization with respect to DTPA extractable elements and available NPK has given promising results. Characterization of CCRs for nutrients has indicated that the CCR is a source of N, P, K, Fe, Cu, Mn and Zn. The study has indicated that the pond ash samples are a source of macro-nutrients and micro-nutrients. Wide variations in the values can be seen in all the parameters that have been studied (Table 2).

Available NPKs are important macro-nutrients in top soil. NPKs along with lime are routinely added to agricultural soils. Similarly, secondary nutrients include Ca and Mg. Calcium is not limiting above pH 5.5. In case of soil with low pH, soils may be deficient in these nutrients. CCRs being rich in these nutrients can be used for improving the nutrient status. Available nitrogen varied from 31.360 (S4) to 87.810 (S2) kg/ha. Available N in case of pond ash samples was high and thus can be used in amending topsoil in agricultural fields.

Available phosphorous varied from 0.52 (S3) to 6.32 (S4) kg/ha. Table 3 gives the fertility rating chart with respect to the available P and available K. Available phosphorous in all the samples was very low 10 kg/ha. From the point of view of nutrient value of phosphorous, pond ash samples are not rich as can be seen from the fertility rating chart.

Available potassium varied from 170.24 (S2) to 358.40 (S1) kg/ha. Fertility rating chart shows that the pond ash samples had medium to high fertility rating. This is also an important macro-nutrient and the pond ash having medium to high potassium concentration can be used in topsoil amendment.

DTPA extractable elements (micro-nutrients and heavy metals) such as iron, copper, manganese, zinc, lead, nickel, chromium, cadmium and cobalt were studied to assess the presence of micro-nutrients in the pond ash samples.

Table 2
Chemical Properties of Pond Ash Samples from a Thermal Power Station of Eastern India

Parameters	Samples			
	S1	**S2**	**S2**	**S4**
pH	6.07	6.46	7.21	6.32
Electrical Conductivity (mmhos/cm)	0.335	0.056	0.140	0.278
Organic Carbon (%)	0.962	1.095	0.610	1.394
Cation Exchange Capacity (meq/100g)	31.74	32.12	32.70	35.60
Macro-nutrients				
Available Nitrogen (kg/ha)	50.716	87.810	50.176	31.360
Available Phosphorus (kg/ha)	1.83	2.50	0.52	6.32
Available K (kg/ha)	358.40	170.24	277.76	259.84
$CaCO_3$ (%)	1.5	1.0	1.0	1.0
Micro-nutrients (Bio-available DTPA Extractable Elements in ppm)				
Fe	9.126	8.926	6.462	9.626
Cu	1.546	0.828	0.734	1.724
Mn	0.824	0.696	1.168	0.643
Zn	2.750	2.454	1.358	2.538
Pb	0.102	0.164	0.106	0.130
Ni	1.074	0.680	0.390	1.576
Cr	BDL	BDL	BDL	BDL
Cd	BDL	BDL	BDL	BDL
Co	0.466	BDL	BDL	0.422
Ultimate Analysis				
Carbon (%)	19.50	9.50	8.40	20.20
Hydrogen (%)	0.61	0.24	0.32	0.40
Sulphur (%)	0.18	0.01	0.37	0.22
Nitrogen (%)	0.41	0.16	0.05	0.11
Oxygen (by diff.) (%)	79.30	90.09	90.86	79.07

Table 3
Fertility Rating Chart

Nutrient	Fertility Status Rating		
	Low	**Medium**	**High**
Organic Carbon (as a measure of available N (%))	<0.5	0.5-0.75	>0.75
Available Phosphorus (kg/ha)	10	10-25	25
Available Potassium (kg/ha)	110	110-280	280

From table 2 one would find that except chromium and cadmium which were reported as below detectable limit (BDL), others like iron copper, manganese, zinc, lead, nickel and cobalt showed their presence in the samples.

Thus, the study shows that the pond ash samples are sources of NPK and micronutrients like iron, copper, manganese, zinc etc. and that they can be used as a source of nutrient in amending soil having such deficiencies Several studies are being cited as examples to show how the ash alone or mixed with soil in different proportions can be used for vegetation growing and also in reclamation of the wasteland.

Conclusion

The experimental study conducted on pond ash samples with respect to the available NPK and bio-available (DTPA) extractable elements has shown that these ashes are source of N, P, K, Cu, Fe, Mn, Zn etc. Such pond ash can become a good source of nutrients in amending the soils having such deficiencies. Further, due to its being alkaline in nature can be effectively used in treating the acidic soils. From the literature review carried out so far, it can be concluded that pond ash (thermal power plant ash) is a source of micro and macro nutrients and can be gainfully utilized in bulk in reclamation of abandoned surface mines and/or overburden dump.

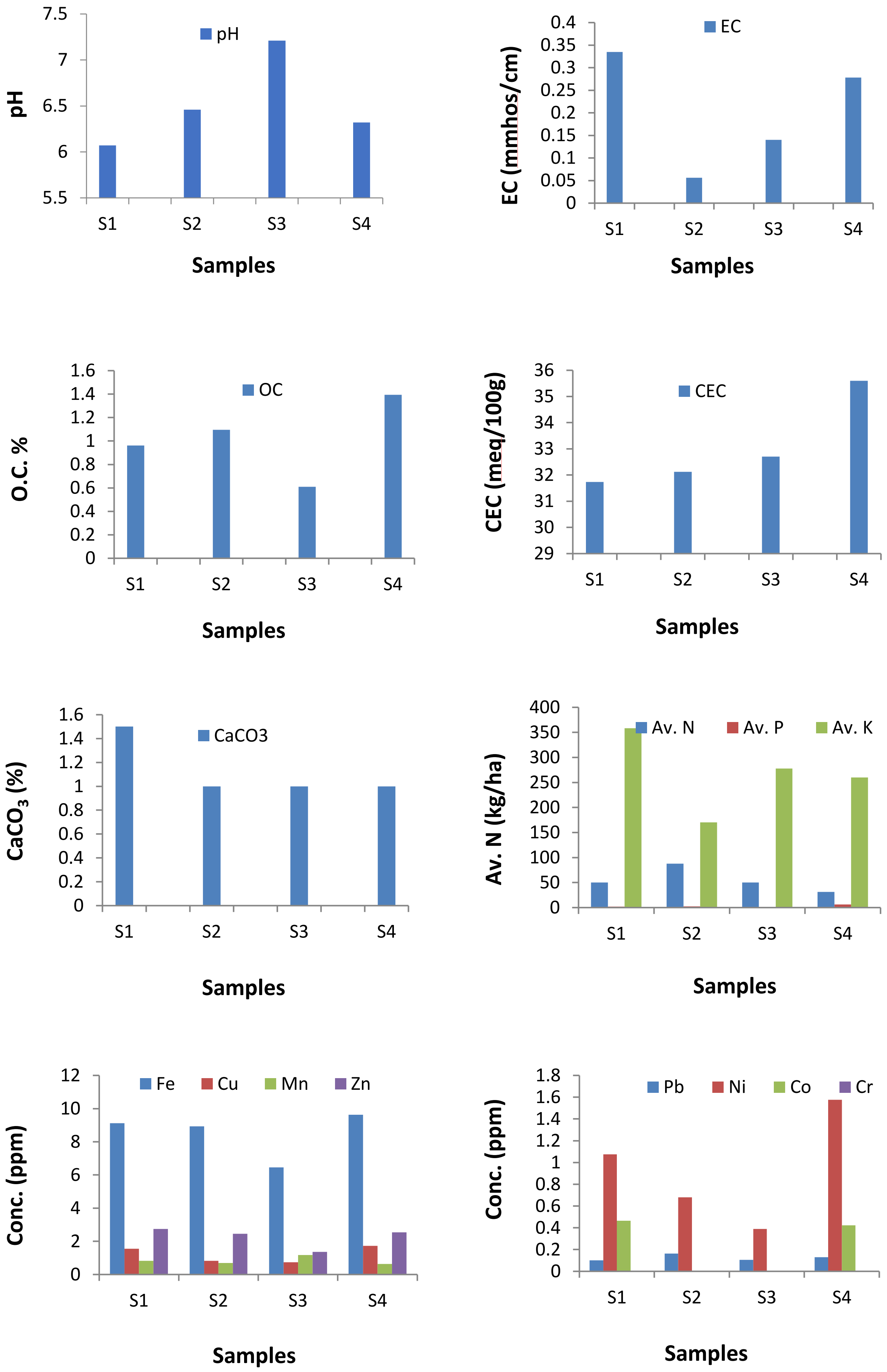

Figure 1: Plot of various chemical parameters for FCI Samples

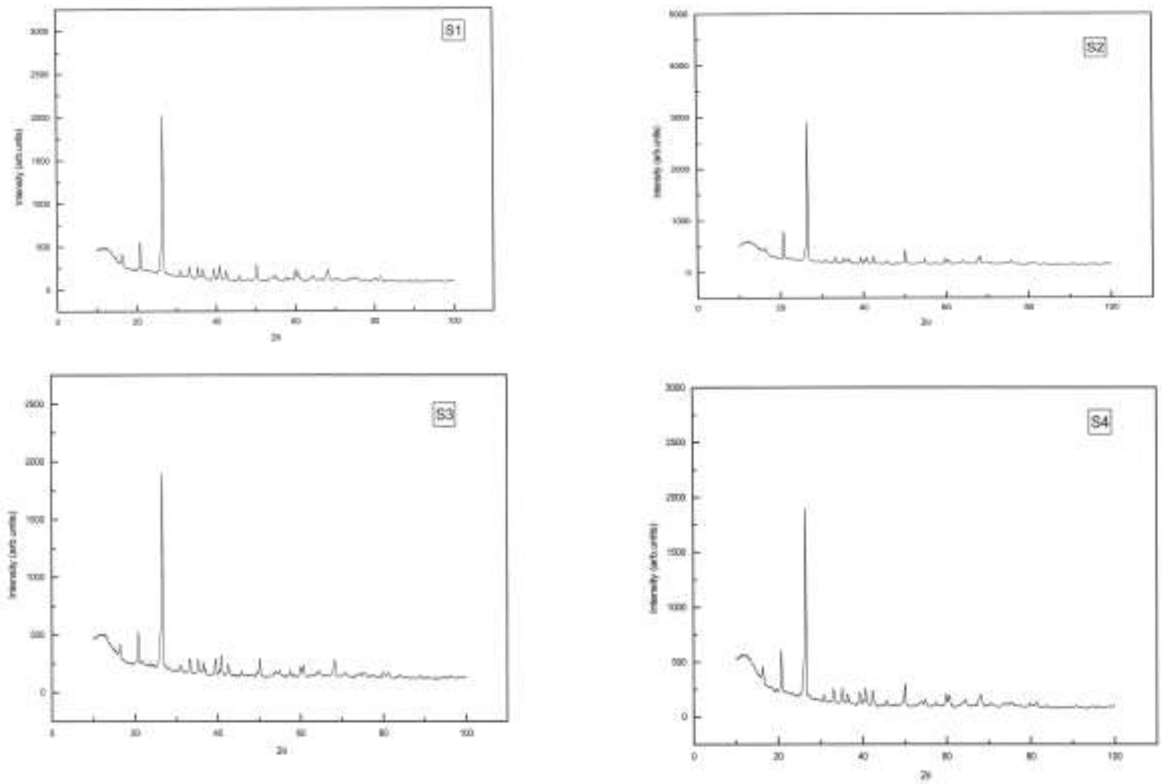

Figure 2: X-ray diffractograms of FCI samples
Note: Quartz (Q) is the most prominent mineral present in the CCR samples as revealed by X-ray diffractograms

Table 4
XRD analysis of Pond Ash Samples from a Thermal Power Station of Eastern India

Plant	Samples	XRD Analysis	
		Major	Minor
FCI	S1	Quartz	Hematite, Mullite
	S2	Quartz	Magnetite, Mullite, Pyrite
	S3	Quartz	Hematite, Mullite
	S4	Quartz	Magnetite, Mullite

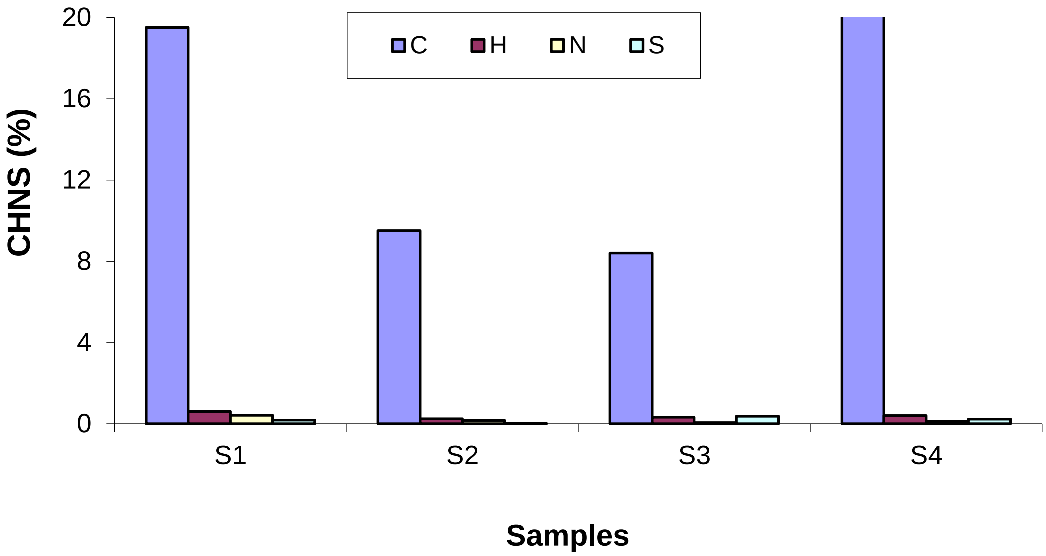

Figure 3: Ultimate analysis of FCI samples

Besides, on the basis of XRD studies, it can be said that such ashes offer highest industrial application potential.

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