Characterization of Coal Combustion Residues using Transmission Electron Microscopy Technique

Abstract

Indian coal-based thermal power stations produces huge amount of coal combustion residues. Proper disposal, management and utilization of these ashes have always been a challenge before the thermal power plant management people. In order to find out the potential use of coal combustion residues one need to explore and look deeply into its various characteristic properties. In the present study the coal combustion residue samples from thermal power station of eastern India were used for characterizing ashes on the basis of Transmission Electron Microscopy technique. The study of the micrographs of Transmission Electron Microscopy showed that the coal combustion residue samples consisted of all the three viz. crystalline, polycrystalline and amorphous phases. The coal combustion residue samples were found to consist of single crystal, single crystal with hexagonal structure, polycrystalline substances and closed packed hexagonal structure. Concentric circles as seen in the diffraction pattern show the presence of polycrystalline substances in the samples. Presence of plerosphere in the coal combustion residue samples can also be seen from some SEM micrographs as well as one of TEM images. XRD studies show the presence of various crystalline substances present in the coal combustion residues. The study shows that the CCR samples are typically formed of Si-Al-Fe system with traces of sodium, potassium, calcium, magnesium, sulphur and titanium.

(Key words: Coal combustion residues, TEM, characterization, thermal power stations)

Introduction

Coal based thermal power plants are today one of the world's most common source of power generation. Today, coal based thermal power generation occupies the largest proportion (more than 75%) of total power produced in India, and due to its wealth of coal reserves the trend would increase in the coming years. More than 190 utility thermal power plants in addition to several captive power plants (CPPs) are operational in India. These power plants uses bituminous coal (with ash content >30%) and producing more than 200 million tonnes of coal combustion residues annually. In the year 2018-2019 217.04 MT of ash was produced out of which 168.40 MT i.e. 77.59% was utilized [1].

Coal combustion residues (CCRs) usually are alumino silicate materials, comprising also Fe, Ca, Mg, Na, K, Ti (primarily in form of an oxide), unburned carbon and other elements in micro or trace concentrations, some of which are toxic or radioactive. A very large number of studies have been conducted in recent years around the world to characterize CCRs in order to estimate its potential environmental impact and understand the importance of CCRs as a material resource for various industrial applications [2,3,5,6,7,8,9].

"The Transmission Electron Microscopy (TEM)[4] is used for the determination of the internal structure of materials, either of biological or non-biological origin. TEM helps in determining whether the material is amorphous, crystalline or poly crystalline quickly and effectively. Besides this TEM can be effectively used in obtaining the lattice parameter information, unit cell details and any periodicity present in the sample arising from structural transformations or ordering processes. It can also be used in determining the presence of super lattice structure that gives information about the long range make up of a material".

TEM materials must be prepared specifically to ensure an appropriate thickness, allowing electrons to pass through the sample; much like light is transmitted conventional optical microscopy through the materials. Because electron wavelength is far lower than that of light, the optimal resolution for TEM images exceeds many orders of magnitude compared to a light microscope. TEM, therefore, can reveal the finest details of internal structure- in some cases as small as the individual atoms.

The energy of the electrons in the TEM determine the relative degree of penetration of the electrons in a specific sample, or alternatively, influence the thickness of material from which useful information can be obtained. Thus a 400 KV provides the highest resolution available and allows for the observation of relatively thick samples (e.g. less than 0.2 micrometers) when compared with the more conventional 100 KV or 200 KV instruments. Because of high spatial resolution obtained, TEM is employed to determine the detailed crystallography of fine-grained, or rare, materials.

Transmission electron microscopy (TEM) studies of CCRs are very limited. Very little literature can be found related to such studies [10]. It should be noted that TEM study can provide very detailed chemical and micro-structural information.

The study presented herein aims to use analytical transmission electron microscopy technique to obtain insight in to the microstructure and possible associated chemical characteristics.

Materials and Methods

Sampling

CCR samples were collected from thermal power station of Fertilizer Corporation of India limited. Samples were collected on five different days over a week and a final homogenized sample was prepared by mixing the appropriate portions.

Principle

The working principle of the instrument is that the electron beam is generated at 50KV at the electron gun of TEM. The electron beam passes through various types of lenses, condenser, objective lens and projector. The transmitted electron beam is passed through the specimen placed in the grid (200 mesh). Electrons pass through a (very thin) sample (i.e. are transmitted) to form an image. After focusing through objective lens, the transmitted electron images are scanned in the fluorescent screen of the TEM.

Methodology

The transmission electron microscopy studies were conducted using Model H-600, Hitachi Instruments Ltd., Tokyo, Japan. The samples were sonicated with methanol solvent in a sonicator machine for an hour. Then the fine dispersed particles were suspended in the medium and a drop of it is placed in a carbon-coated grid (200 mesh) by micropipette. Then the grid was placed in the specimen holder of the TEM and then evacuated. Then an electron beam operated at 50 KV voltage is transmitted through the sample and the electron micrograph and diffraction pattern was recorded. From the electron micrograph we measure the particle size and nature. This is done by measuring the grain size by scale and divided by magnification. From the diffraction patterns we observe and infer the phase characteristics of the sample e.g., crystalline, polycrystalline and amorphous nature.

Results and Discussion

The micrographs of transmission electron microscopy (TEM) are shown in Figure 1. The study of the micrographs shows that the CCR samples consisted of all the three crystalline, polycrystalline and amorphous phases. The substances consisted of single crystal, single crystal with hexagonal structure, polycrystalline substances and closed packed hexagonal structure. Concentric circles as seen in the diffraction pattern show the presence of polycrystalline substances in the samples. Presence of plerospheres in the CCR samples can also be seen from the micrographs (Figure 1-f).

TEM is being used as an efficient tool to study the microstructure, shape and surface texture. The phase information of the crystallographic structure can be found out from TEM images. In Figure 1 (a, c & d) concentric circles shows the presence of polycrystalline morphology in CCR samples. In Figure 1(b) somewhat diffused rings can be seen which is the characteristics of amorphous morphology. Figure 1(e) represents crystalline nature with single crystal. Plerosphere presence in the CCR samples can be seen from figure 1(f). The presence of plerosphere is also supported from the SEM micrographs as shown in Figure 2. Figure 3 also shows the diffractograms of the CCR samples under study. Table 1 shows the major and minor substances present in the CCR samples. Quartz was found as the major substance and the minor components included magnetite, hematite, pyrite and mullite. Table 2 gives the results on energy dispersive x-ray analysis (EDXA). The study shows that the CCR samples are typically formed of Si-Al-Fe system with traces of sodium, potassium, calcium, magnesium, sulphur and titanium.

Table 1: XRD Analysis of CCR Samples from Fertilizer Corporation of India Limited

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

Table 2: Summary of EDXA (%) of CCR Samples from Fertilizer Corporation of India Limited

Plant	Samples	Si	Al	Fe	Na	K	Ca	Mg	S	Ti
FCI	S1	26.10	14.28	1.98	-	1.27	0.31	0.55	-	1.39
	S2	21.51	13.17	11.91	-	0.94	0.50	0.23	-	1.14
	S3	25.78	15.59	2.84	-	1.45	0.72	0.25	-	1.16
	S4	26.59	14.40	2.54	-	1.26	0.35	0.65	-	1.73

Conclusion

TEM is a very versatile analysis technique. Many different types of analysis can be performed (hardware dependent). Complimentary information can be obtained from distinct small (nm) regions allowing full nano-scale characterisation. In the present study the visual observation of the micrographs of TEM shows that the CCR samples consist of all the three phases' viz. crystalline, polycrystalline and amorphous. The presence of polycrystalline substances was confirmed owing to the presence of the concentric circles. The substances also consisted of single crystal, single crystal with hexagonal structure, polycrystalline substances and closed packed hexagonal structures. Spheres within a sphere were also observed in some micrographs showing the presence of plerospheres in the CCR samples. These findings from this study are also supported through studies done by SEM-EDXA and XRD.

References

1. Annual Report 2018-19. Central Electricity Authority January 2020. Report on Fly Ash Generation at Coal/Lignite Based Thermal Power Stations and its Utilization in the Country for the Year **2018-19**. Retrieved from https://cea.nic.in/wp-content/uploads/2020/04/flyash_201819.pdf.

2. Bayat, O., Characterization of Turkish Fly Ashes, *Fuel*, **77**, 1059–1066 **(1998)**

3. Goodarzi, F., Characteristics and Composition of Fly Ash from Canadian Coal-fired Power Plants, *Fuel*, **85**, 1418-1428 **(2006)**

4. Graef, Marc de, Introduction to Conventional Transmission Electron Microscopy, Cambridge University Press, Cambridge **(2003)**.

5. Iyer, R. S. and Scott, J. A., Power Station Fly ash – A Review of Value-added Utilization outside of the Construction Industry, *Resources, Conservation and Recycling*, **31(3)**, March, 217-228 **(2001)**.

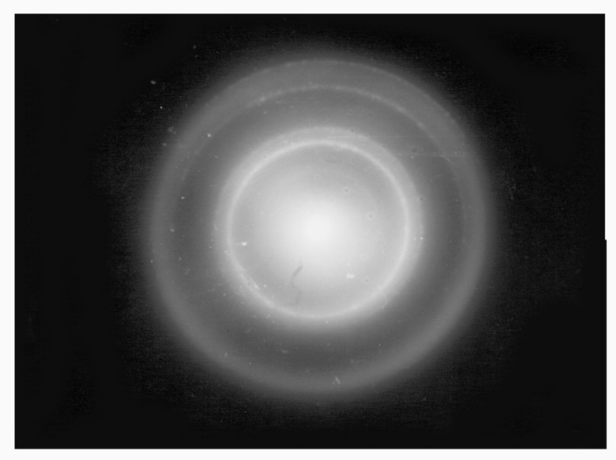
6. Kostakis, G., Characterization of the Fly Ashes from the Lignite Burning Power Plants of Northern Greece based on their Quantitative Mineralogical Composition, *Journal of Hazardous Materials*, **166**, 972–977 **(2009)**.

7. Kumar, R., Sharma, S., Kumar, A. and Arora, C., Coal Combustion Residues Characterization using Scanning Electron Microscopy & Energy Dispersive X-ray (SEM-EDXA) Analysis, **3**(2), 60-72 (**2020**). DOI 10.24294/can.v3i2.595

8. Howladar, F. M. and Islam, R., Md., A Study on Physico-chemical Properties and uses of Coal Ash of Barapukuria Coal Fired Thermal Power Plant, Dinajpur, for Environmental Sustainability, *Energ. Ecol. Environ.*, **1(4)**, 233–247, (**2016**). DOI 10.1007/s40974-016-0022-y

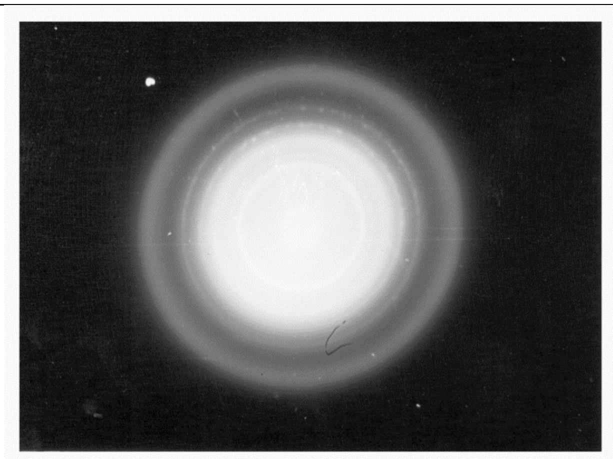
9. Sarkar, A., Vishwakarma, S., Banichul, H., Mishra, K. K. and Roy, S. S., A Comprehensive Analysis of the Particle Size and Shape of Fly Ash from Different Fields of ESP of a Super Thermal Power Plant, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, **34(5)**, 385-395 (**2012**). DOI: 10.1080/15567031003614649

10. Hashimoto, T., Takai, K., Nguyen, H.V.Q, Nomura, M. and Ishihara, A. Analysis of Thermal Behavior of Crystalline Minerals in Bituminous Coal Samples under Air and Argon Atmospheres, *ACS Omega*, 6, 1197–1204 (**2021**). DOI 10.1021/acsomega.0c04311

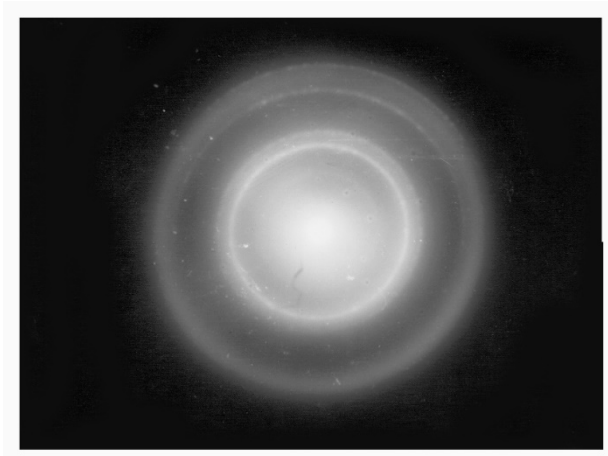


(a)

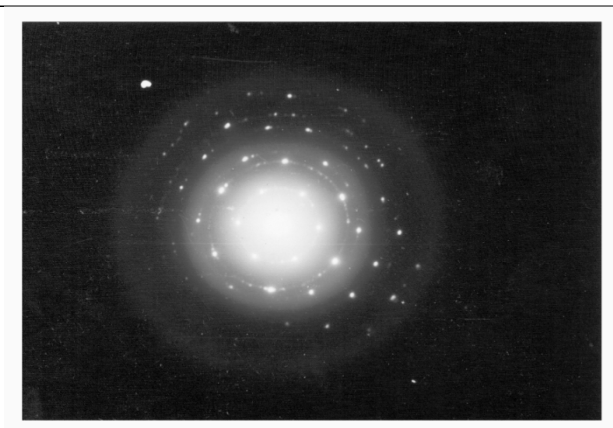
(b)



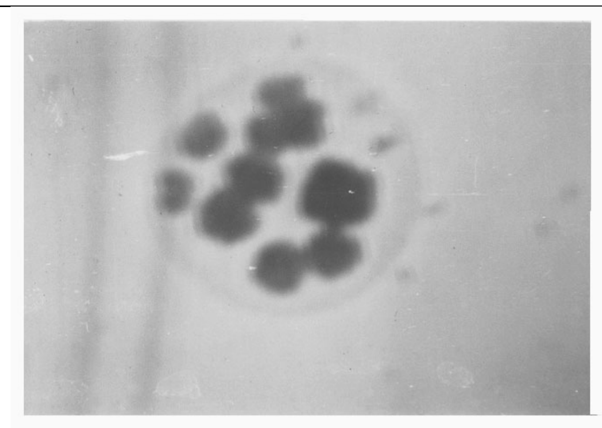
(c)



(d)



(e)



(f)

Figure 1: Transmission Electron micrographs of CCR Samples

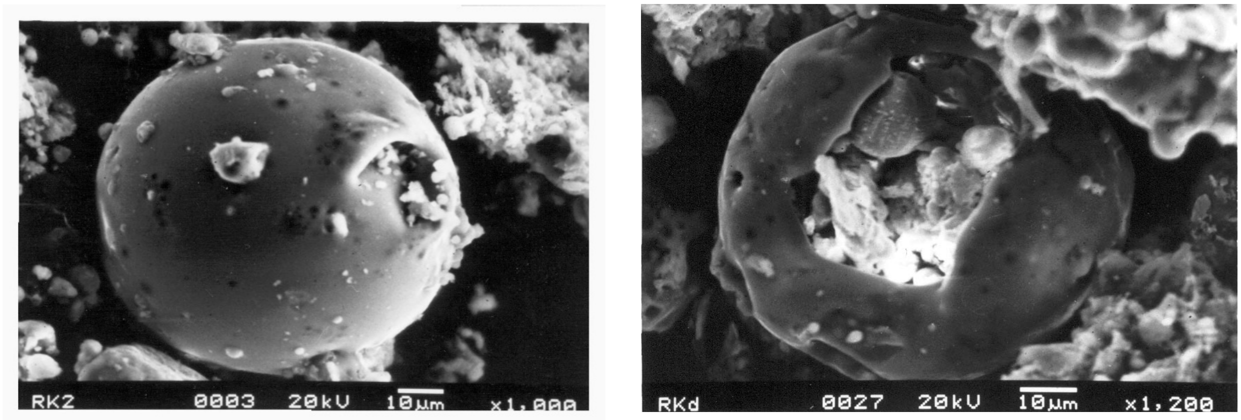
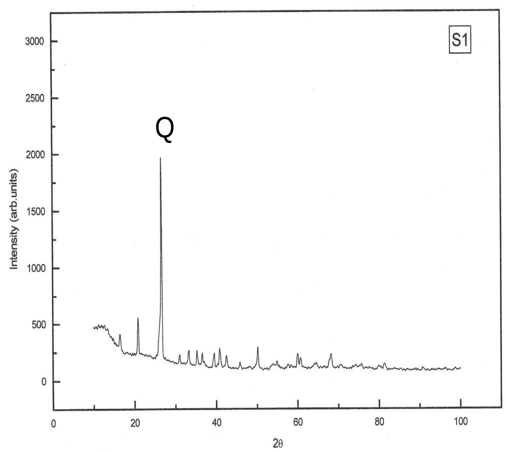
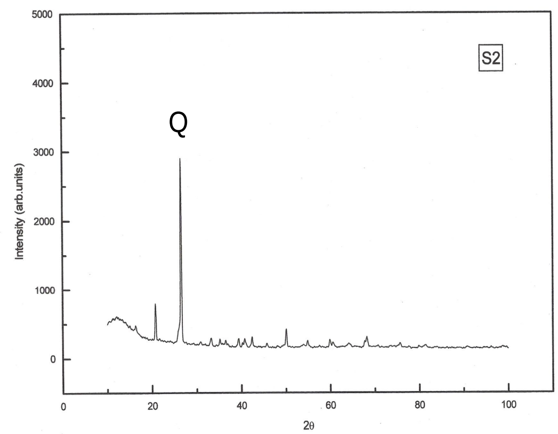


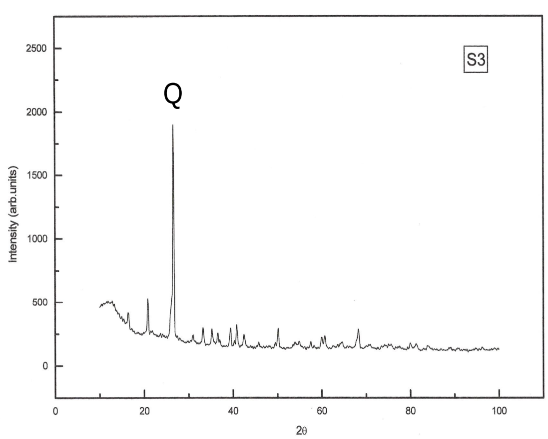
Figure 2: SEM Micrographs showing the plerospheres presence in the CCR Samples



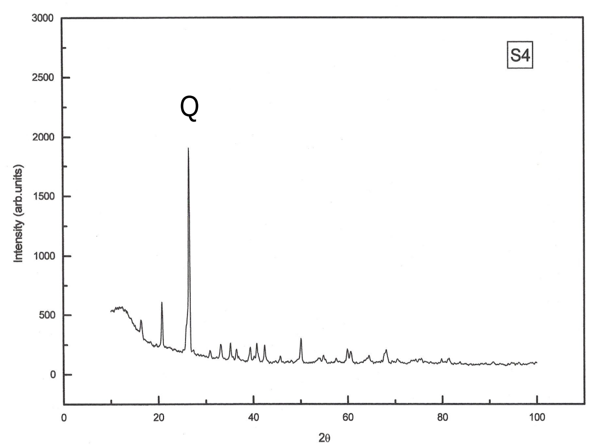
(i)



(ii)



(iii)



(iv)

Figure 3: X-Ray Diffractograms of FCI CCR Samples

Note: Quartz (Q) is the most prominent mineral present in the CCR samples as seen in X-ray diffractograms.