From Waste to Resource: Elemental Characterization of Fly Ash Using EDXRF

Sunit Kumar Singh*, G. D. Vani, Pranay Sharma, Anil Kumar Das

EDXRF Lab, NTPC Energy Technology Research Alliance, NTPC Ltd., Greater Noida, India
sksingh27@ntpc.co.in

Abstract. Energy Dispersive X-ray Fluorescence Spectroscopy (EDXRF) is a powerful, non-destructive analytical technique employed to determine the elemental composition of various materials. It operates by bombarding a sample with high-energy X-rays, which causes the emission of secondary (fluorescent) X-rays unique to each element. These emitted X-rays generate an energy spectrum that serves as a distinct fingerprint, enabling the qualitative identification of elements present in the sample. Furthermore, the intensity of these characteristic X-rays is directly proportional to the elemental concentration, allowing for accurate quantitative analysis. This technique is particularly valuable in analyzing coal fly ash, where the elemental composition plays a crucial role in defining its properties, environmental behavior, and possible industrial applications. Fly ash composition affects the strength and durability of concrete when used as a partial substitute in Portland cement. In addition, elemental analysis can reveal the presence of economically significant components such as rare earth elements, opening opportunities for resource recovery and sustainable waste utilization. A detailed understanding of the elemental makeup also supports the development of innovative uses, including wastewater adsorbents and materials for carbon capture and storage.

Keywords: Energy Dispersive X-ray Fluorescence Spectroscopy (EDXRF), X-rays, elemental composition, Fly ash, Waste management.

1 Introduction

1.1 Energy Dispersive X-ray Fluorescence Spectroscopy (EDXRF)

Electromagnetic radiant energy propagates through space as waves that span a wide range of frequencies and wavelengths, collectively forming the electromagnetic spectrum (Figure 1A). Radiant energy waves with wavelengths ranging from 0.01 to 10 nm and frequencies between 3×10^{16} Hz and 3×10^{19} Hz are classified as X-rays [1].

X-ray fluorescence (XRF) spectroscopy is a non-destructive analytical technique widely used for determination of the elemental composition of materials. In this technique, the sample is irradiated with high-energy X-rays, which excite its constituent

S. Shaswattam et al. (eds.), *NTPC Transactions on Energy Research (NTER 2025)*,
https://doi.org/10.2991/978-94-6463-849-3_15

atoms and cause them to emit secondary (fluorescent) X-rays. These emitted X-rays have characteristic energies specific to the elements in the sample, enabling their identification and analysis (Figures 1A and 1B) [2]. The spectrometer separates the beam components with different energies. It measures the energy intensities inside narrow energy arrays. In EDXRF, the dispersion of beam components is performed directly within the detector. The associated electronics also play a key role in this process. This setup generates an energy-dependent signal for each absorbed X-ray photon.

Energy-dispersive detectors are typically based on semiconductor technology. The energy of each detected X-ray corresponds to the identity of the emitting element, while the intensity (i.e., the number of detected X-rays) is directly proportional to the concentration of that element. The processed signals are displayed as an energy spectrum, where X-ray counts are plotted against X-ray energy, typically measured in kiloelectron volts (keV). Each peak in the spectrum corresponds to a specific element in the sample, and the intensity of the peak indicates its relative abundance [3], [4].

1.2 Coal Fly Ash (CFA)

In power plants, CFA is a by-product of coal combustion. During the combustion process, the coal burns to produce energy. The mineral impurities in coal, such as clay, quartz, feldspar, and other silicate minerals, do not combust. These impurities are left behind as ash. This ash is then collected as CFA. The fine particles that rise with flue gases are called fly ash, which is typically collected using electrostatic precipitators or other filtration systems. The composition of CFA raises environmental concerns due to the presence of heavy metals and trace elements. These can pose risks if not properly managed, such as groundwater contamination or air pollution through dust [5], [6].

The composition of CFA varies based on the type of coal used, combustion conditions, and other influencing factors. Among the primary components of fly ash is silica and alumina. Silica (SiO_2) constitutes 20-60%, alumina (Al_2O_3) constitutes 15-30%, Iron oxide (Fe_2O_3) constitutes 5-15%, Calcium oxide (CaO) constitutes 1-30%, Magnesium oxide (MgO) constitutes 1-5%, Titanium dioxide (TiO_2) typically varies from 1% to 2%, and Sodium oxide (Na_2O) and Potassium oxide (K_2O) are typically in the range of 0.5% to 5%.

In addition to these major oxides, CFA can contain trace amounts of elements which include heavy metals such as arsenic (As), mercury (Hg), lead (Pb), chromium (Cr), and cadmium (Cd). Other than heavy metals, Rare earth elements (REEs) elements like cerium (Ce), neodymium (Nd), and yttrium (Y) are found in small quantities [5].

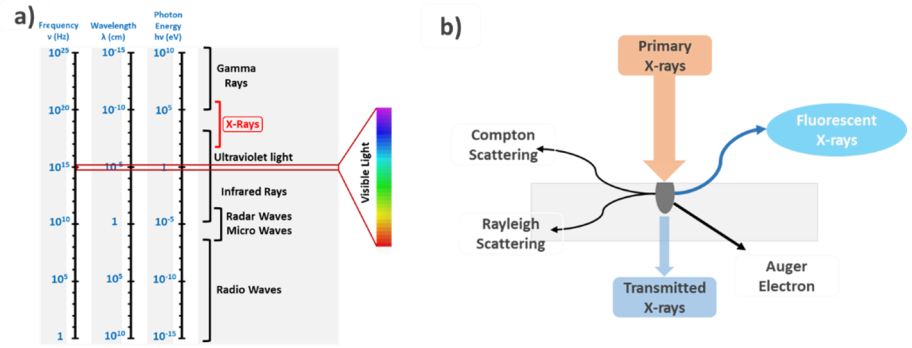

Fig. 1. a) Electromagnetic spectrum of light, b) X-rays interacting with a substance.

2 XRF Equipment in NETRA, NTPC Ltd.

The Xenemetrix EDXRF EX-6600, employed at NETRA, NTPC Ltd., is an EDXRF spectrometer specifically designed for elemental analysis of a wide range of materials (Figure 2) [7]. This X-ray fluorescence (XRF) system offers versatility in detecting elements from sodium (Na) to uranium (U), covering a broad concentration range—from trace levels in parts per million (ppm) up to 100%. It is equipped with a high-power X-ray tube, operating at up to 50 kV and 50 W, which generates the primary X-rays necessary for exciting atoms in a sample. Certain configurations feature a silver (Ag) anode for enhanced performance. The system employs Silicon Drift Detectors (SDD), known for their exceptional resolution, rapid data acquisition, and high count rate capability, enabling precise measurements even within complex sample matrices. Advanced calibration software supports both semi-quantitative and fully quantitative analysis, incorporating intuitive user interfaces and sophisticated correction algorithms to address challenges such as matrix effects and inter-element interferences. Additionally, the system enables multi-channel analysis, allowing the simultaneous detection and measurement of multiple elements, making it highly efficient for comprehensive elemental profiling.

Calibration and quantitative analysis are reinforced by the use of certified Standard Reference Materials (SRMs) supplied by the National Institute of Standards and Technology (NIST), including SRM 2691, SRM 2690, SRM 2689, and SRM 1633b. These SRMs, rigorously tested and accompanied by Certificates of Analysis detailing certified values, measurement methods, and traceability to the International System of Units (SI), ensure accuracy, precision, and traceability in scientific and industrial applications. Comparative analyses of elemental oxide concentrations in these SRMs against values obtained using the XRF system confirm strong alignment with NIST standards, underscoring the reliability and performance of the instrument. Table 1 shows wt% concentration of elements in their oxide forms as specified in certificate of analysis provides by NIST versus the concentration evaluated in NETRA for same SRM samples. The results are in congruence with the NIST standard values.

Table 1. Elemental Quantification Data (in wt% Concentration) comparing NIST SRM values with data generated in Laboratory for same standards using Xenematrix EDXRF.

Elements (in Oxide form)	SRM							
	2691		2690		2689		1633c	
	NIST (wt%)	NETRA (wt%)	NIST (wt%)	NETRA (wt%)	NIST (wt%)	NETRA (wt%)	NIST (wt%)	NETRA (wt%)
Na_2O	1.46 ± 0.06	1.37 ± 0.21	0.32 ± 0.02	0.34 ± 0.15	0.33 ± 0.01	0.38 ± 0.14	0.23 ± 0.01	0.23 ± 0.13
MgO	5.17 ± 0.13	4.23 ± 0.11	2.53 ± 0.08	2.28 ± 0.06	1.01 ± 0.08	0.93 ± 0.04	0.82 ± 0.08	0.90 ± 0.04
Al_2O_3	18.531 ± 0.73	18.15 ± 0.09	23.32 ± 0.52	23.11 ± 0.10	24.44 ± 0.39	24.17 ± 0.11	25.08 ± 1.15	25.93 ± 0.11
SiO_2	35.99 ± 0.25	36.06 ± 0.11	55.29 ± 0.36	56.29 ± 0.14	51.46 ± 0.17	50.86 ± 0.14	45.56 ± 1.12	49.07 ± 0.14
P_2O_5	1.16 ± 0.04	1.05 ± 0.02	1.19 ± 0.02	0.89 ± 0.02	0.22 ± 0.02	0.15 ± 0.01	0.43 ± 0.02	0.29 ± 0.01
SO_3	2.07 ± 0.12	2.14 ± 0.02	0.37 ±0.02	0.38 ± 0.00	Not Given	0.82 ± 0.01	0.27 ± 0.04	0.55 ± 0.01
K_2O	0.40 ± 0.01	0.43 ± 0.01	1.25 ± 0.04	1.23 ± 0.01	2.65 ± 0.04	2.87 ± 0.01	2.13 ± 0.07	2.09 ± 0.01
CaO	25.81 ± 0.44	27.18 ± 0.09	7.98 ± 0.18	8.119 ± 0.03	3.04 ± 0.08	3.16 ± 0.01	1.90 ± 0.05	1.87 ± 0.01
TiO_2	1.50 ± 0.03	1.52 ± 0.01	0.86 ± 0.01	0.91 ± 0.01	1.25 ± 0.16	1.31 ± 0.01	1.21 ± 0.05	1.24 ± 0.01
MnO	0.02 ± 0.01	0.07 ± 0.01	0.03 ± 0.01	0.04 ± 0.002	0.03 ± 0.01	0.03 ± 0.002	0.03 ± 0.004	0.03 ± 0.002
Fe_2O_3	6.32 ± 0.04	6.47 ± 0.02	5.10 ± 0.08	5.58 ± 0.02	13.32 ± 0.08	14.34 ± 0.05	15.00 ± 0.55	16.91 ± 0.06

Table 2. PT test results.

S. No.	PT Parameters	Observation 1	Observation 2	Avg. (X)	Total participants	Assigned Value ($X_{assigned}$)	σ (Standard Deviation)	Z score
1	Al_2O_3,%	28.73	28.78	28.76	13	28.39	1.47	0.24
2	CaO,%	1.52	1.54	1.53	13	1.48	0.20	0.24
3	Fe_2O_3,%	5.10	4.92	5.01	12	4.81	0.265	0.71
4	LoI,%	0.35	0.37	0.36	13	0.32	0.0564	0.67
5	MgO,%	0.84	0.87	0.86	13	0.78	0.0771	0.98
6	SiO_2,%	60.00	60.25	60.13	13	60.81	1.32	-0.49
7	SO_3,%	0.12	0.13	0.13	13	0.17	0.0058	-0.68

Fig. 2. Xenematrix EDXRF Model EX-6600.

Proficiency testing (PT) and Z-scores are crucial for validating analytical results, ensuring accuracy, and maintaining quality control in laboratory testing. A Z-score evaluates a laboratory's performance in a PT by measuring the deviation of its result from the assigned value, calculated as:

$$Z = \frac{X - X_{assigned}}{\sigma}$$

where X is the laboratory's result, $X_{assigned}$ is the assigned or consensus value, and σ is the standard deviation of PT results. In PT, a Z-score determines result acceptability: $|Z| \leq 2.0$ is satisfactory, indicating compliance with acceptable limits; $2.0 < |Z| \leq 3.0$ is questionable, requiring further review; and $|Z| > 3.0$ is unsatisfactory, necessitating immediate corrective action. The PT test on fly ash samples was conducted in collaboration with Global PT Provider Pvt. Ltd., New Delhi, and the results are presented in Table 2.

3 Sample analysis using EDXRF

The samples selected here for discussion are different variety of sample received from NTPC stations regularly for analysis of elemental composition of their ash after combustion. Sample are received in different categories such as coal (before combustion), CFA (from boiler of thermal power plant), Bottom Ash, Clinker, and other alternate boiler fuels. Alternated fuel includes biomass sourced from paddy, wheat straw, rice husk, pine needle and municipal solid waste. EDXRF spectra of these samples are shown in Figure 3. The spectra are collected in the range 0 to 10 keV. The elements (with their characteristics X-Ray wavelength energy) estimated in this range are Na (1.041 keV), Mg(1.254 keV), Fe(6.403 keV), Al(1.487 keV), Si(1.740 keV),

K(3.313 keV), P(2.015 keV), Ca(3.691 keV), Ti(4.510 keV), S(2.308 keV) and Mn(5.898 keV).[8]

Table 3 shows the detailed elemental quantification in oxide form for the above discussed samples. As can be seen from Table 3, Alumina content in the first four samples varied in the range 24-29 wt%, Iron varied in the range 4-8 wt% and Silica varied in the range 59-61.5 wt% which is not much variation. Overall, all other element showed minor variation. Torrified charcoal showed significant difference in quantities of these elements. Silica (11.95 wt%) and alumina (52.82 wt%) is found in lower values than coal with significant increase in alkaline metals Mg (4.98 wt%) and Ca (14.99 wt%). Biomass generally have variations in elemental composition compared to coal. Biomass is characterized by lower levels of alumina and more level of alkaline earth metals (Table 3). Calcium and magnesium are vital for plant growth and cellular functions. Calcium is essential for maintaining cell wall structure and stability, while magnesium serves as a central component of chlorophyll, the molecule responsible for photosynthesis. Plants actively absorb these minerals from the soil as they grow, leading to relatively high concentrations of Ca and Mg in plant tissues, and thus in biomass derived from these plants. As plant material transforms into coal, it undergoes intense heat, pressure, and chemical reactions that change its composition. This process, called coalification, drives off water and volatile organic compounds, and leads to a concentration of carbon while reducing some mineral content. Thus, elements like Ca and Mg can either volatilize, dissolve, or integrate into other mineral structures in coal, resulting in their relatively lower levels compared to raw biomass [9], [10]. The elemental composition of Municipal Solid Waste (MSW) ash varies depending on the type of waste processed, combustion conditions, and local waste management practices. However typically, the composition of MSW ash is closer to biomass than coal as can be observed in Table 3. Mill-rejected coal (Table 3) refers to coal that is considered unsuitable for combustion due to quality concerns. Excessive ash content lowers combustion efficiency and contributes to issues such as slagging, fouling, and increased maintenance. Slagging occurs when molten ash deposits accumulate on boiler surfaces, reducing heat transfer and raising energy consumption. Fouling happens when ash particles adhere to heat exchanger tubes, decreasing efficiency and causing blockages. High levels of SiO_2 and Al_2O_3 make ash highly refractory, meaning it melts at elevated temperatures and forms hard, sticky deposits. Iron oxide interacts with other minerals, such as calcium and sulfur, to create low-melting-point compounds that produce sticky ash, which readily adheres to boiler tubes. Elevated Fe_2O_3 content lowers the ash fusion temperature, further increasing the likelihood of slagging and fouling.

The calcium (Ca) and silicon (Si) content in fly ash play pivotal roles in determining its suitability for various applications. These elements influence the reactivity, strength, and durability of materials in which fly ash is used, particularly in construction and environmental applications. High-Ca fly ash (Class C fly ash) has a high lime content ($CaO \geq 20\%$) that enables it to exhibit self-cementing behavior when mixed with water, forming hydration products like calcium silicate hydrate (C-S-H) and calcium aluminate hydrate (C-A-H) [11]. This property makes it suitable for direct use as a binder in road bases, soil stabilization, and low-strength construction applications. Even, Low-Ca fly ash (Class F fly ash) can contribute to pozzolanic reactions when

mixed with lime or Portland cement, enhancing strength over time. A balanced combination of Si (for pozzolanic activity) and Ca (for early strength) is ideal. High-Ca fly ash accelerates early strength gain, while high-Si fly ash ensures long-term strength and durability. Calcium reacts with silica (SiO_2) and alumina (Al_2O_3) in the presence of water to form additional cementitious products [12, 13]. High-Ca fly ash is effective in neutralizing acidic environments, such as mine tailings or acidic wastewater, due to its alkaline nature. It is also used for immobilizing heavy metals in contaminated soils by forming stable calcium complexes. Even, Al compounds in fly ash adsorb and immobilize contaminants, making it effective in environmental applications [14]. High-Si fly ash is a preferred raw material for geopolymers, where silica reacts with an alkaline activator to form a three-dimensional aluminosilicate network, yielding materials with excellent mechanical and chemical properties [15,16].

Table 3. Elemental Analysis of samples using EDXRF received from NTPC Stations.

Oxides	*Na_2O*	*MgO*	*Al_2O_3*	*SiO_2*	*P_2O_5*	*SO_3*	*K_2O*	*CaO*	*TiO_2*	*MnO*	*Fe_2O_3*
Samples						**Wt%**					
Coal	0.21 ±0.09	0.94 ±0.04	28.25 ±0.11	59.39 ±0.15	0.20 ±0.01	0.44 ±0.01	1.09 ±0.01	1.19 ±0.01	1.94 ±0.02	0.031 ±0.001	5.59 ±0.02
Fly Ash	0.101 ±0.027	0.61 ±0.04	27.57 ±0.11	60.63 ±0.15	0.20 ±0.01	0.21 ±0.004	1.06 ±0.01	1.51 ±0.01	2.03 ±0.02	0.032 ±0.001	4.45 ±0.02
Bottom Ash	0.097 ±0.012	0.51 ±0.04	27.72 ±0.12	60.38 ±0.17	0.17 ±0.01	0.07 ±0.003	0.91 ±0.01	0.59 ±0.01	2.37 ±0.02	0.038 ±0.002	6.13 ±0.03
Clinker	0.118 ±0.012	0.70 ±0.04	24.03 ±0.11	61.19 ±0.16	0.32 ±0.01	0.05 ±0.003	1.32 ±0.01	1.06 ±0.01	1.80 ±0.02	0.037 ±0.001	7.99 ±0.03
Torrified Charcoal	1.694 ±0.687	4.98 ±0.14	11.95 ±0.07	52.82 ±0.13	1.25 ±0.03	0.97 ±0.01	4.02 ±0.03	14.99 ±0.06	0.63 ±0.01	0.039 ±0.002	5.46 ±0.03
Biomass Paddy	4.558 ±0.923	2.56 ±0.07	5.89 ±0.06	67.45 ±0.16	0.73 ±0.02	2.63 ±0.03	8.39 ±0.04	4.89 ±0.02	0.16 ±0.003	0.047 ±0.001	2.02 ±0.01
Biomass Wheat Straw	0.141 ±0.015	3.94 ±0.10	5.69 ±0.06	45.66 ±0.15	7.56 ±0.18	11.26 ±0.11	9.75 ±0.02	10.51 ±0.05	0.30 ±0.01	0.064 ±0.004	4.19 ±0.02
Biomass Rice Husk	0.229 ±0.049	1.05 ±0.03	6.52 ±0.06	80.03 ±0.16	0.82 ±0.02	0.37 ±0.01	2.91 ±0.02	2.89 ±0.02	0.31 ±0.004	0.039 ±0.001	4.46 ±0.02
Biomass Pine Needle	0.239 ±0.058	10.70 ±0.19	6.61 ±0.06	26.00 ±0.11	5.57 ±0.08	2.77 ±0.03	7.05 ±0.02	35.82 ±0.13	0.31 ±0.01	0.069 ±0.001	4.46 ±0.03
Municipal Solid Waste	1.296 ±0.159	6.46 ±0.19	12.94 ±0.08	42.65 ±2.36	2.36 ±1.38	1.38 ±0.02	2.98 ±0.02	22.36 ±0.08	1.09 ±0.01	0.048 ±0.002	5.58 ±0.03
Mill Rejected Coal	0.312 ±0.067	0.25 ±0.01	9.94 ±0.06	38.21 ±0.11	0.02 ±0.01	1.63 ±0.02	1.05 ±0.01	1.12 ±0.01	0.36 ±0.004	0.025 ±0.001	46.27 ±0.25

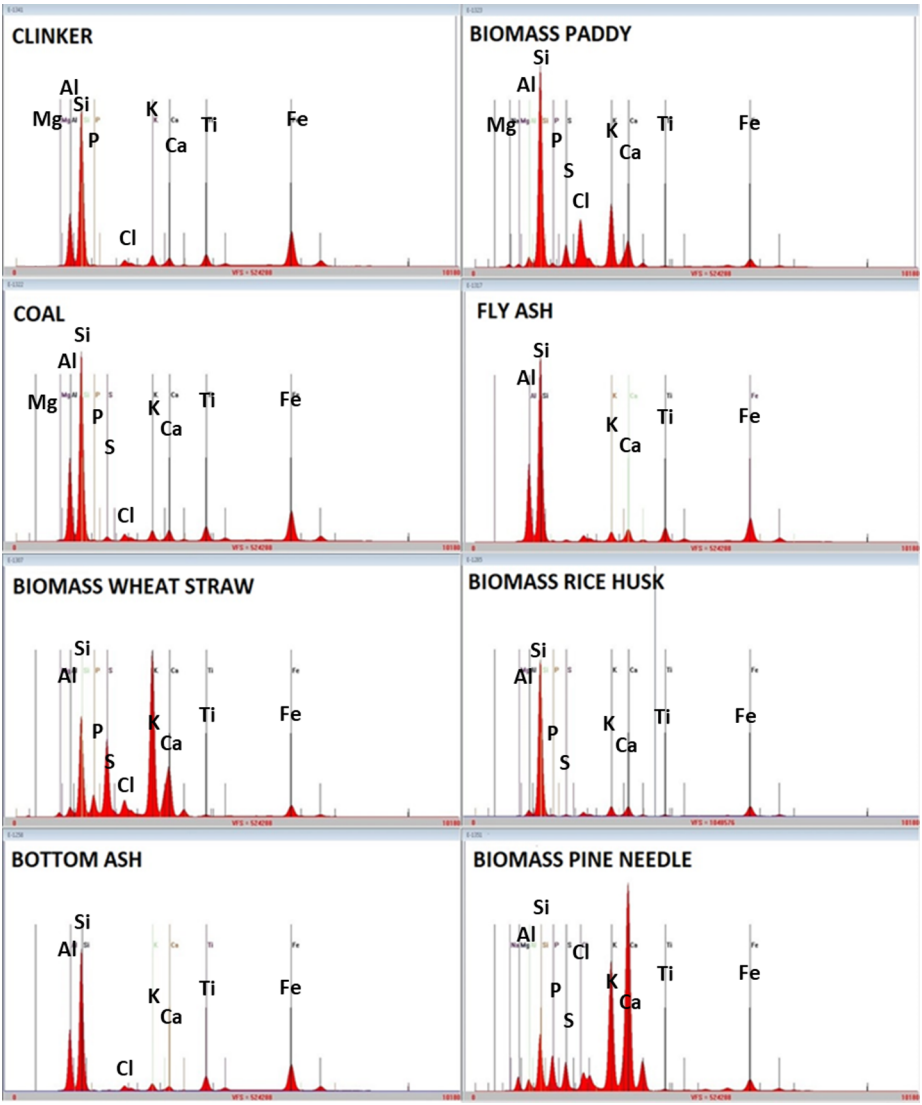

Fig. 3. EDXRF Spectra of different sample received from NTPC stations.

4 Conclusion

EDXRF is a powerful technique in elemental analysis, widely used for its non-destructive nature, rapid results, and ability to analyze a wide range of elements in various sample types. It can analyze solids, liquids, powders, and thin films. This versatility allows it to be used across different industries. Unlike some other analytical techniques, EDXRF requires minimal preparation. Samples can be analyzed as is, saving time and reducing the potential for contamination or loss of material. EDXRF can simultaneously detect multiple elements in a single measurement, making it highly efficient for routine analysis and quality control processes where speed is critical. It provides both qualitative (identifying which elements are present) and quantitative (determining their concentrations) results. This makes it useful for material characterization and quality assurance in manufacturing and production.

In NTPC, CFA is a byproduct generated during the combustion of coal. The large-scale production of CFA poses significant environmental and management challenges. Without proper control measures, fly ash particles can become airborne and pose significant health risks, such as respiratory problems and lung diseases. Significant research is being conducted to find sustainable ways to handle fly ash and convert it into valuable products. This requires regular monitoring of elemental composition of the ash where EDXRF has been pivotal in quality monitoring and control.

Acknowledgments

The authors gratefully acknowledge NETRA, NTPC Ltd. for providing the laboratory facilities essential for carrying out this work. Special thanks are extended to the Executive Director, NETRA, for the kind support and encouragement provided to the analytical laboratories.

Disclosure of Interests

The authors declare that they have no competing interests.

References

1. Attix, Frank H.: Introduction to Radiological Physics and Radiation Dosimetry. WILEY-VCH Verlag GmbH & Co. KGaA, (1986).
2. What is X-ray fluorescence (XRF), HORIBA. Available at: https://www.horiba.com/usa /scientific/technologies/energy-dispersive-x-ray-fluorescence-ed-xrf/what-is-x-ray-fluorescence-xrf/ (last accessed: 2024/10/08).
3. Penner-Hahn, J. E.: Handbook of X-ray Spectrometry, 2nd ed., Revised and Expanded Edited by René E. Van Grieken (University of Antwerp) and Andrzej A. Markowicz (Vienna, Austria). Marcel Dekker, Inc: New York and Basel (2002).
4. Newbury, D. E.: Standardless Quantitative Electron-Excited X-ray Microanalysis by Energy-Dispersive Spectrometry: What Is Its Proper Role? In Microscopy and Microanalysis (Vol. 4, Issue 6, pp. 585–597). Oxford University Press (OUP). (1998).

5. Mathapati, M., Amate, K., Durga Prasad, C., Jayavardhana, M. L., Hemanth Raju, T.: A review on fly ash utilization. In Materials Today: Proceedings (Vol. 50, pp. 1535–1540). Elsevier BV (2022).
6. Izquierdo, M., Querol, X.: Leaching behavior of elements from coal combustion fly ash: An overview. In International Journal of Coal Geology 94, 54–66 (2012).
7. Xenematrix NexT Series Operational Manual, EX-3600M/66000 XRF Spectrometers, D/N 0160805200101, Revision 5.0, Feb 2009.
8. Thompson, A., et al.: X-ray Data Booklet. Lawrence Berkeley National Laboratory, University of California. (2009) https://xdb.lbl.gov/, (last accessed: 2024/10/12).
9. Vassilev, S. V., Baxter, D., Andersen, L. K., Vassileva, C. G. An overview of the chemical composition of biomass. Fuel 89(5), 913–933 (2010).
10. Dai, S., Ren, D., Zhou, Y., Chou, C.-L., Wang, X., Zhao, L., Zhu, X.: Mineralogy and geochemistry of a superhigh-organic-sulfur coal, Yanshan Coalfield, Yunnan, China: Evidence for a volcanic ash component and influence by submarine exhalation. Chemical Geology 255(1–2), 182–194 (2008).
11. Chindaprasirt, P., Rattanasak, U.: Calcium wastes as an additive for a low calcium fly ash geopolymer. Scientific Reports, 13(1), 16351 (2023).
12. Yadav, V. K., Fulekar, M. H.: Advances in methods for recovery of ferrous, alumina, and silica nanoparticles from fly ash waste. Ceramics, 3(3), 384-420 (2020).
13. Kelechi, S. E., Adamu, M., Uche, O. A. U., Okokpujie, I. P., Ibrahim, Y. E., Obianyo, I. I.: A comprehensive review on coal fly ash and its application in the construction industry. Cogent Engineering, 9(1), 2114201 (2022).
14. Aughenbaugh, K. L., Stutzman, P., Juenger, M. C.: Assessment of the glassy phase reactivity in fly ashes used for geopolymer cements. Geopolymer Binder Systems, 1566, 11-20 (2013).
15. Peng, X., Tonglin, Z.: Comprehensive utilization of high alumina coal fly ash under the recyclable economy model. Ind. Chem, 4, 128 (2018).
16. Alterary, S. S., Marei, N. H.: Fly ash properties, characterization, and applications: A review. Journal of King Saud University – Science, 33, 6, 101536 (2021).