

Characterization of Coal Ash Including Fly Ash Particles

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KEYWORDS

Coal combustion products (CCPs), cenospheres, energy X-ray dispersive spectrometry (EDS), flue gas desulfurization material (FGD), plerospheres, phase contrast microscopy (PCM), polarized light microscopy (PLM), scanning electron microscopy (SEM), transmission electron microscopy (TEM)

ABSTRACT

Particles of coal ash can be distinguished from other dust particles based on optical microscopy examination and electron microscopy analysis. This paper provides some background information about coal ash/fly ash and augments the information in the published literature about the particle characteristics as determined by light and electron microscopy. The authors also describe a method for determining the number of fly ash particles per unit area of surface dust.

INTRODUCTION

According to the U.S. Environmental Protection Agency, coal combustion products (CCPs) are the materials produced during the process of burning coal in thermal power plants. CCPs include coal ash (bottom ash and fly ash), boiler slag and flue gas desulfurization material (FGD) (1). As suggested by their names, bottom ash is the residue ash that falls to the bottom of the furnace during the combustion of coal, while fly ash consists of particles that are carried up the stack

in the flue gas. Boiler slag is the molten bottom ash collected at the base of the slag tap and cyclone type furnaces after the molten slag comes in contact with quenching water. Boiler slag is generally described as a black granular material made up of hard, black, angular particles that have a smooth, glassy appearance. FGD materials are generated during the reduction of SO₂ emissions from the exhaust gas streams of coal-fired boilers. The physical and chemical forms of the FGD materials depend on the particular process used to reduce the SO₂ in the exhaust gas. Dry powdered FGD material may contain sulfites and/or sulfates. A common FGD material consists of small fine particles of gypsum. Particles of coal ash may also be found in some FGD materials.

Fly ash is a high temperature combustion product generated at temperatures of 1,500 °C to 1,750 °C. The chemical composition and structure of fly ash particles vary and depend on the composition of coal that generate them and the amount of time and the temperature to which the particles are exposed in the exhaust stream. Although fly ash can contain particles of partially combusted coal, it is generally described as the spherical particles of the fine powder made largely of alumina, silica and other trace oxides.

Investigations of coal ash in environmental settings can involve finding the fly ash particles (generally the spherical portion) that have been released from a coal-fired boiler stack. In addition to inadvertent flue gas releases, fly ash may be introduced into the environment from settling ponds that lose their integrity. Fly ash particles can also be released into the environ-

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Table 1. Major Morphological Classes of Coal Ash Particles*

Non-Spherical Coal Ash	
Class	Description
A	Amorphous, non-opaque (silicate)
B	Amorphous opaque (silicate)
C	Amorphous mixed opaque and non-opaque (silicate/coal/iron oxide)
D	Rounded, vesicular, non-opaque (silicate/coal/iron oxide)
E	Rounded vesicular, mixed opaque and non-opaque
F	Angular, lacy, opaque (carbonaceous)
Spherical Coal Ash	
Class	Description
G	Non-opaque, cenosphere (hollow sphere)
H	Non-opaque, plerosphere (sphere packed with other spheres)
I	Non-opaque, solid spheres (white-yellow-orange-deep red-brown)
J	Opaque, sphere (black-iron-magnetic)
K	Non-opaque sphere with either surface or internal crystals
L	Frosted or frothy

*Classes A-K based on Fisher, 1978 (6). Class L is based on present study.

ment through the degradation of commercial products that use the recycled particles. Fly ash has been used to improve the workability of concrete and increase its compressive strength in cement or structural fill (2).

CHARACTERIZATION AND IDENTIFICATION OF FLY ASH/COAL ASH PARTICLES

Particles of coal ash have been characterized by a number of researchers by their morphology (size and shape) and elemental composition using light and electron microscopy (3–11).

Ramsden and Shibaoka (8) characterized individual coal ash/fly ash particles from Australian coal-fired power stations by a combination of optical microscopy, electron microscopy and quantitative electron microprobe analysis. They recognized seven categories of coal ash:

1. Unfused detrital minerals (principally quartz).
2. Irregular spongy particles derived from partly fused clay minerals.
3. Vesicular colorless glass (in the form of irregular particles and cenospheres) derived from viscous melts.
4. Solid glass (mostly in the form of spherical par-

ticles and sometimes pigmented) derived from fluid melts.

5. Dendritic iron oxide particles (mostly spherical) containing variable amounts of glass matrix.
6. Crystalline iron oxide particles (mostly spherical) containing minimal amounts of glass.
7. Unburned char particles.

Natusch (9) suggested four major classifications of fly ash particles:

1. Non-spherical clinker.
2. Solid spheres, either clear or opaque.
3. Hollow glass spheres (cenospheres).
4. Hollow glass spheres filled with smaller spheres (plerospheres).

Fisher et al. (6) described 11 major morphological classes of coal ash particles as determined by light microscopy. These include opaque and non-opaque, spherical and non-spherical particles. Table 1 lists the various classes we found, including those derived by Fisher. The 11 Fisher classes are generally similar to the seven categories recognized by Ramsden and Shibaoka. Hand-drawn images in the Fisher article (6) illustrate the relationship between coal ash particle type and the combustion process. In a similar way, the PLM and SEM micrographs from six samples

displayed in McCrone's *Particle Atlas* (5) show the effect of time and temperature in the formation of coal ash. The images range from unburned coal particles to glassy spheres.

MATERIALS AND METHODS

Samples of coal ash/fly ash were obtained from a number of coal-fired power plants. In addition, a sample of Standard Reference Fly Ash (NIST-SRM 2689) was obtained from the National Institute of Standards and Technology. The NIST SRM 2689 is a blend of three fly ashes, which are products of western Kentucky, Colorado and Wyoming coals and were obtained from three different coal-fired power plants.

The examination of the samples for coal ash/fly ash was performed initially by stereomicroscopy and then polarized light microscopy (PLM). The light microscopy was augmented with top-light illumination (reflected light) that allowed the various colors exhibited by the fly ash particles to be observed. Scanning electron microscopy (SEM) coupled with an energy X-ray dispersive spectrometry (EDS) system was used to determine the elemental composition of representative particles. Automated SEM was used to determine the size distribution of one sample.

RESULTS

The fly ash particles analyzed in this study were colorless, yellow, orange, red, green, blue, purple and black in reflected light. Figure 1, based on a table in Fisher's article (6), illustrates the concept with actual coal ash images. Figures 2–12 show light microscope photomicrographs of representative coal ash particles for each of the 11 Fisher classifications. Figure 13 shows a representative particle of a 12th class, a frothy sphere type, found in some fly ash samples.

Several characteristics of the coal ash particles from rough and irregular (Figure 14) to smooth spheres (Figure 15) are illustrated by examination with SEM-EDS. Some non-spherical particles are smooth (Figure 16). Some spheres are bumpy (Figure 17) and some are etched (Figure 18). Plerospheres are identified by the smaller spheres within them (Figures 19 and 20). The primary elements present in the fly ash spheres as determined by the X-ray analysis are aluminum, silicon, magnesium and, in some cases, iron. Varying smaller amounts of potassium, phosphorous, titanium, calcium and sulfur may also be present. The ranges of SEM X-ray spectra found in one fly ash sample are shown in Figure 21–29.

See Figures 2–29 on pages 78–84.

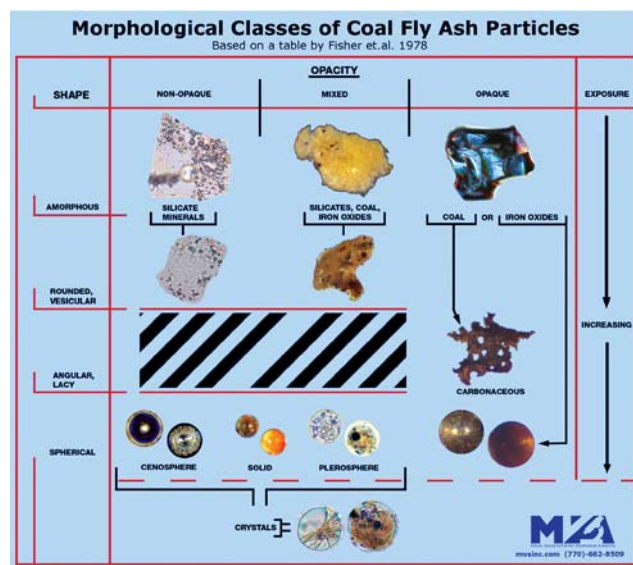


Figure 1. Morphological classes of coal fly ash characterized by Fisher et al. (6) and photographed using PLM by Millette et al.

The particle size distribution of fly ash particles in the NIST reference fly ash sample, as analyzed by automated scanning electron microscopy (ASEM), is shown in Table 2. Note that while the percentage of fly ash particles less than 2.5 μm in diameter is 1% by mass, the percentage of fly ash particles less than 2.5 μm in diameter is 62.7% by particle number.

MEASURING THE AMOUNT OF COAL ASH/FLY ASH IN AIR AND SURFACE DUST

In 1980, a method for determining the concentration of fly ash particles per volume of air collected on standard membrane filter air cassettes was proposed by Presswood et al. (12). This air monitoring procedure uses a modified version of the phase contrast microscope method P&CAM 239 (13), the precursor to NIOSH 7400. The method counts spheres in the size range of 0.75 μm to 15 μm under 400x magnification with phase contrast illumination. A calibrated Porton reticle is used to size the spheres and to define the field of view in the microscope. The concentration of spherical particles per cubic centimeter of air is calculated by multiplying the number of spheres found times the effective area of the filter divided by the number of fields of view, the area of the field of view, and the volume of air collected. Because phase contrast microscopy (PCM) cannot identify particles, this moni-

**Table 2. Automated SEM Analysis:
Percentages of Fly Ash Particles by Number and Mass***

Particle Diameter (μm)	Number (%)	Mass (%)*
0.5 – <1.0	24.6	0.1
1.0 – <2.5	38.6	0.7
2.5 – <5.0	21.5	3.5
5.0 – <7.5	2.5	7.3
7.5 – <10.0	2.3	10.9
= or >0.0	6.5	77.4

Total number of particles: 2,127

*All fly ash particles are assumed to have essentially the same density.

toring procedure is used after the dust has been generally characterized by PLM.

Wipe sampling can be used to determine the surface loading of coal ash per unit area by using the fly ash particles as an indicator. A wipe sample is collected from a measured area using a polyester clean-room wipe. The entire wipe sampler is placed in a beaker with particle-free water and sonicated using a sonic bath for 15 minutes to release the particulate from the wipe. An aliquot of known amount is withdrawn from the beaker and filtered onto a 0.2 μm pore size polycarbonate filter. A portion of the filter is placed directly on a microscope stub and carbon coated for electrical conductivity. The filter portion is then analyzed at a magnification of 1,000x with an SEM coupled with an EDS. Fly ash particles are identified, sized and recorded. Either 25 fly ash particles larger than 0.5 μm are counted or 50 fields of view are examined for each sample. Each suspect fly ash particle is analyzed by EDS and its diameter determined. The total number of fly ash particles per area of the original sampled surface is calculated using the following equation:

$$\text{Particles per cm}^2 = (\# \text{ particles} \times \text{effective area of filter}) / (\# \text{ fields of view} \times \text{area of field of view} \times \text{aliquot proportion} \times \text{area sampled})$$

Fly ash surface loading levels are determined for three diameter ranges: greater than 10 μm, between 10 μm and 2.5 μm, and less than 2.5 μm. A study of three independent analysts analyzing the same sample showed a relative standard error of approximately 11% for a loading in the range of 3,600 fly ash particles per cm².

DISCUSSION AND CONCLUSIONS

The numerous characterizations of coal ash particles into different classes by previous researchers have been confirmed in the present study, with the addition of one class: the frothy sphere type. In addition to the 11 Fisher classes (6) identified using PLM, several surface characteristics were determined with SEM that could be used for classification, including irregular, rough or etched surfaces to smooth, spherical shapes. The chemical composition data determined by EDS found the primary component of coal ash to be an aluminosilicate structure with varying amounts of magnesium and iron, and small amounts of trace elements and metals. The elemental data we determined were generally consistent with those reported by Mishra et al. (14), who concluded: "The major constituents of fly ash are identical to earthy materials such as soil and shales. While the oxides of iron, calcium, aluminum, silicon and magnesium constitute about 98%–99% of the composition of fly ash, other elements such as potassium, sodium, titanium, chromium, cobalt, etc. occur only in traces. Sometimes the improper or incomplete combustion results in the presence of significant amount of carbon in the fly ash matrix." The range of chemical compositions of coal ash determined in our analysis provides a base for future research in environmental studies dealing with the inadvertent release of coal combustion products.

The particle sizing distribution analysis for a NIST fly ash sample was performed using ASEM and showed that 62.7% of particles were less than or equal to 2.5 μm in diameter. However, the sample preparation methods for particle sizing analysis vary. While the Presswood method (12) described earlier is suffi-

cient for monitoring particles after the coal ash dust has been characterized by PLM, the use of PCM may be problematic due to the inherent difficulty in particle identification. We proposed a different method using SEM instead of PCM to calculate the number of particles per area of the original sampled surface. The ability to distinguish individual particles using SEM together with EDS may provide a more significant aid to environmental studies involving air and water contamination by coal ash.

REFERENCES

1. U.S. Environmental Protection Agency. Coal Combustion Products, <http://www.epa.gov/wastes/conserve/imr/ccps/> (accessed July 24, 2012).
2. Brady, G.S. and Clauser, H. R. *Materials Handbook*, 12th Ed., McGraw-Hill Book Co.: New York, p 170, 1986.
3. Block, C. and Dams, R. "Study of Fly Ash Emissions During Combustion of Coal," *Environmental Science & Technology*, **10**, pp 1011–1017, 1976.
4. Davison, R.L., Natusch F.S. and Wallace J.R. "Trace Elements in Fly Ash," *Environmental Science & Technology*, **8**, pp 1107–1113, 1974.
5. McCrone, W.C. et al. *The Particle Atlas – PAE²*, Electronic Edition, Microdataware, pp 569–574, 1992.
6. Fisher, G.L., Prentice, B.A., Silberman, D., Ondov, J.M., Blermann, A.H., Ragaini, R.C. and McFarland, A.R. "Physical and Morphological Studies of Size-Classified Coal Fly Ash," *Environmental Science & Technology*, **12** (4), pp 447–451, 1978.
7. Fisher, G.L., Chang, D.P.Y. and Brummer, M. "Fly Ash Collected from Electrostatic Precipitators: Microcrystalline Structures and the Mystery of the Spheres," *Science*, **192**, pp 553–555, 1976.
8. Ramsden A.R. and Shibaoka, M. "Characterization and Analysis of Individual Fly-Ash Particles from Coal-Fired Power Stations by a Combination of Optical Microscopy, Electron Microscopy and Quantitative Electron Microprobe Analysis," *Atmospheric Environment*, **16** (9), pp 2191–2206, 1982.
9. Natusch, D.F.S. "Characterization of Atmospheric Pollutants from Power Plants," in *Second Federal Conference on the Great Lakes*, Great Lakes Basin Commission: Ann Arbor, MI, pp 114–129, 1976, as described in Gibbon, D.L. "Microcharacterization of Fly-Ash and Analogs: the Role of SEM and TEM," *Scanning Electron Microscopy*, SEM Inc.: AMF O'Hare (Chicago), IL, 1979.
10. Gibbon, D.L. "Microcharacterization of Fly-Ash and Analogs: the Role of SEM and TEM," *Scanning Electron Microscopy*, SEM Inc.: AMF O'Hare (Chicago), IL, 1979.
11. Dudas, M.J. and Warren, C.J. "Submicroscopic Model of Fly Ash Particles," *Geoderma* **40**, pp 101–114, 1987.
12. Presswood, W.G., Huyser, J. and Whitaker, C.G. "Monitoring Airborne Fly Ash by the Membrane Filter Counting Procedure," *American Industrial Hygiene Association Journal*, **41**, pp 33–39, 1980.
13. P&CAM 239. *NIOSH Manual of Analytical Methods*, 2nd Ed., U.S. Dept. of HEW, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health: Cincinnati, OH, Vol. 1, 1977.
14. Mishra, C.D., Pandey, H.D., Prasad, B. and Mediratta, S.R. "A Method For Rapid Characterization of Fly Ash," in *Residues and Effluents*, Reddy, R.G., Imrie, W.P. and Queneau, P.B., eds., Proceedings of the International Symposium, San Diego, CA, March 1–5, 1992; The Minerals, Metals and Materials Society: Warrendale, PA, pp 149–155, 1992.

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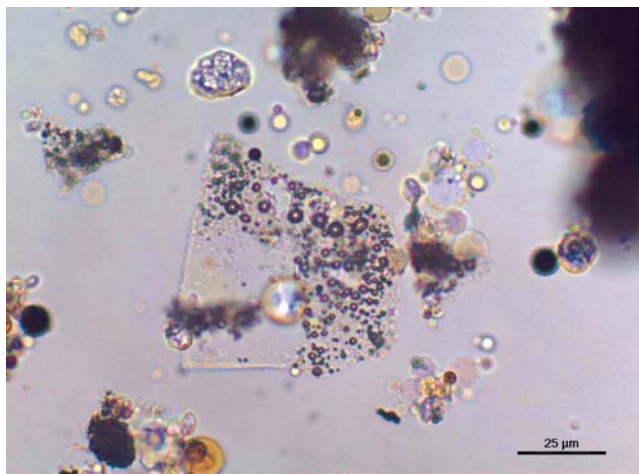


Figure 2. Amorphous, non-opaque; Class A.

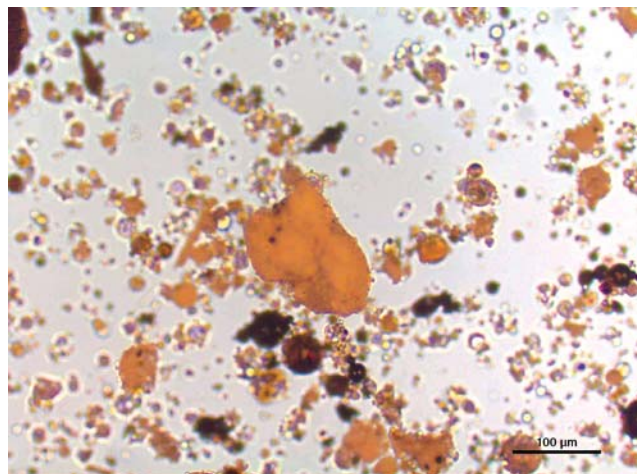


Figure 3. Amorphous, opaque; Class B.

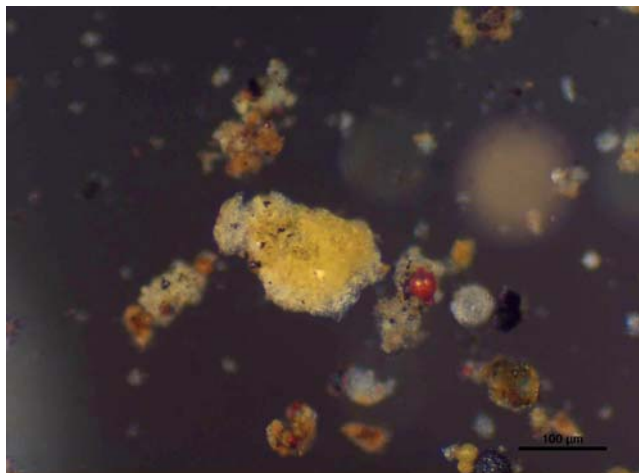


Figure 4. Amorphous, mixed opaque and non-opaque; Class C.

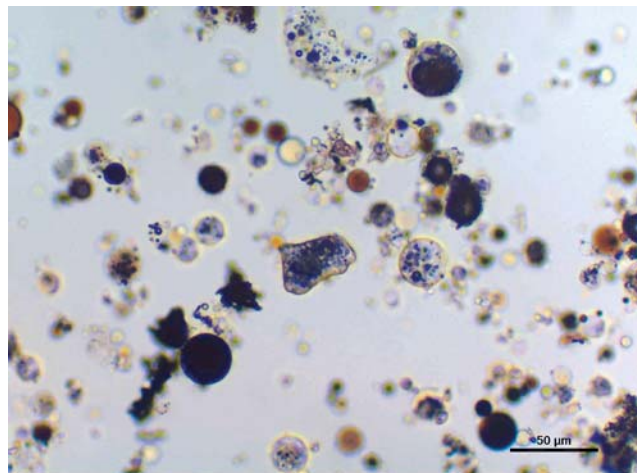


Figure 5. Rounded, vesicular, non-opaque; Class D.

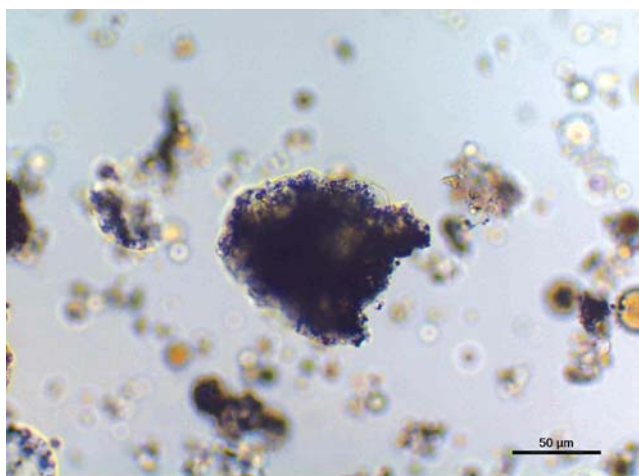


Figure 6. Rounded, vesicular, mixed; opaque and non-opaque; Class E.

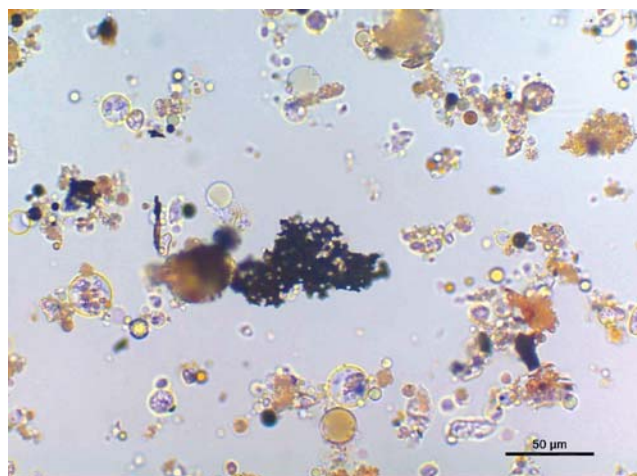


Figure 7. Angular, lacy, opaque, carbonaceous; Class F.

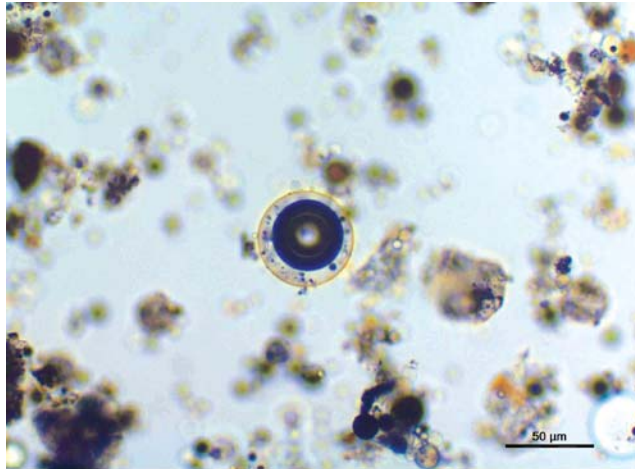


Figure 8. Non-opaque cenosphere; Class G.

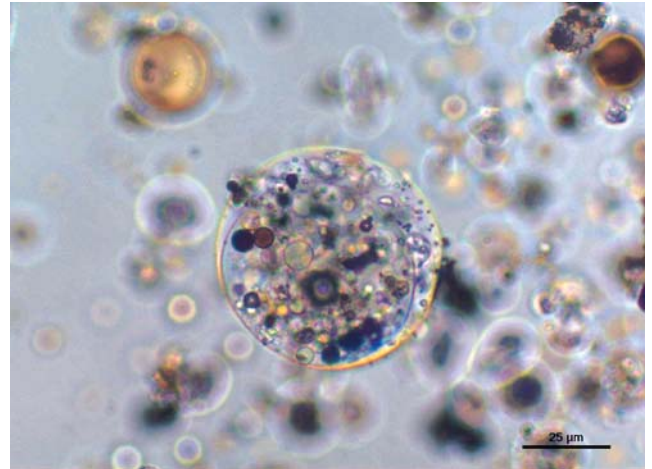


Figure 9. Non-opaque plerosphere; Class H.

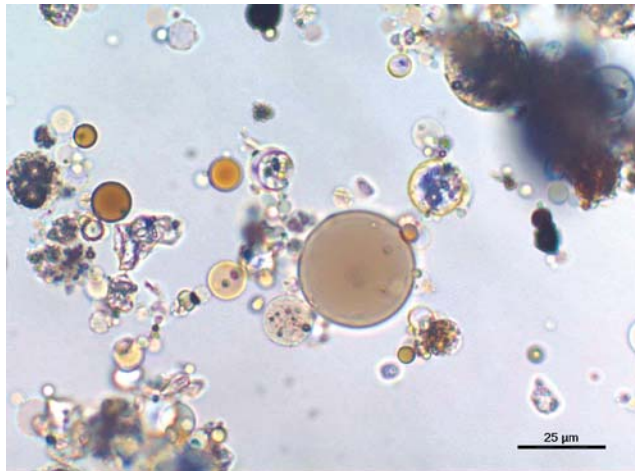


Figure 10. Non-opaque solid sphere; Class I.

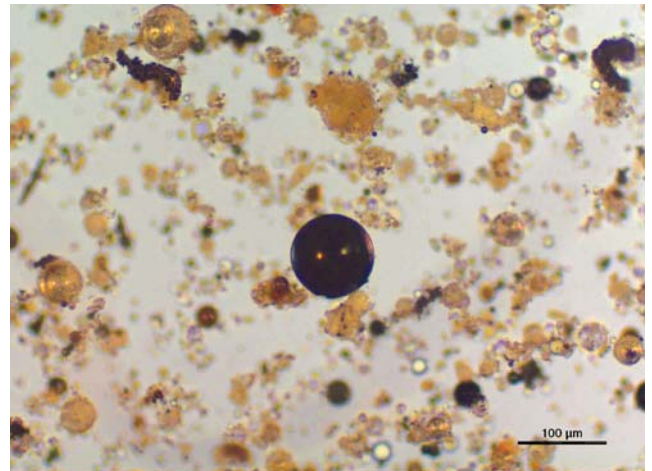


Figure 11. Opaque sphere; Class J.

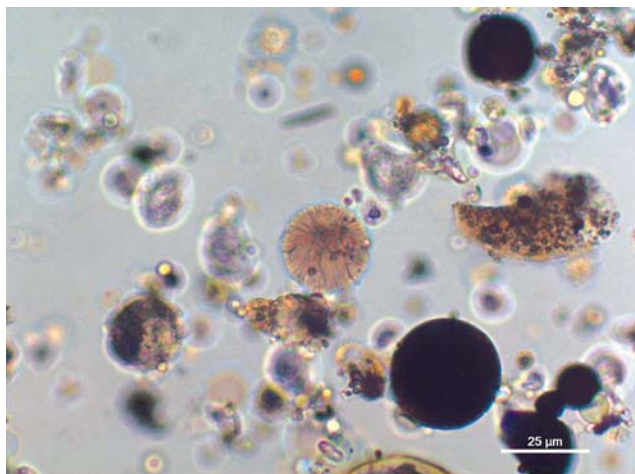


Figure 12. Non-opaque sphere containing crystals; Class K.

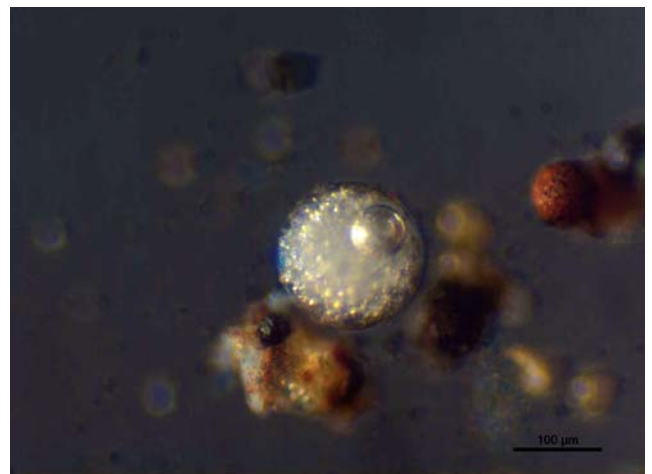


Figure 13. Frosted or frothy sphere; Class L.

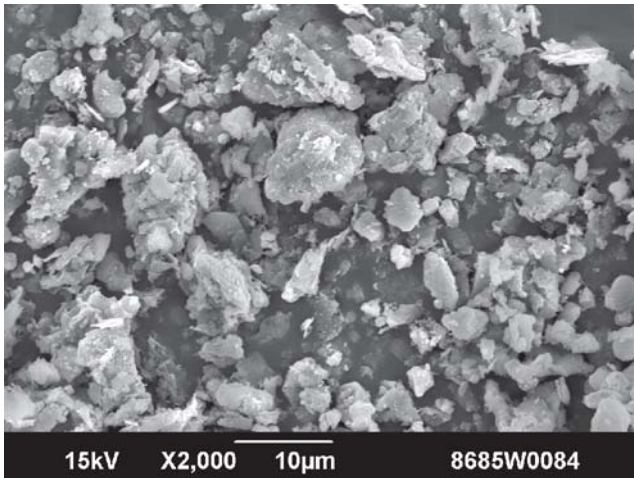


Figure 14. Irregular, rough coal ash particles.

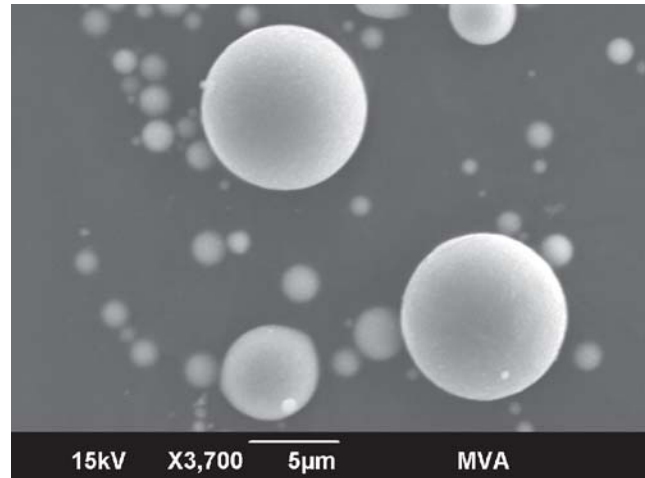


Figure 15. Smooth fly ash spheres.

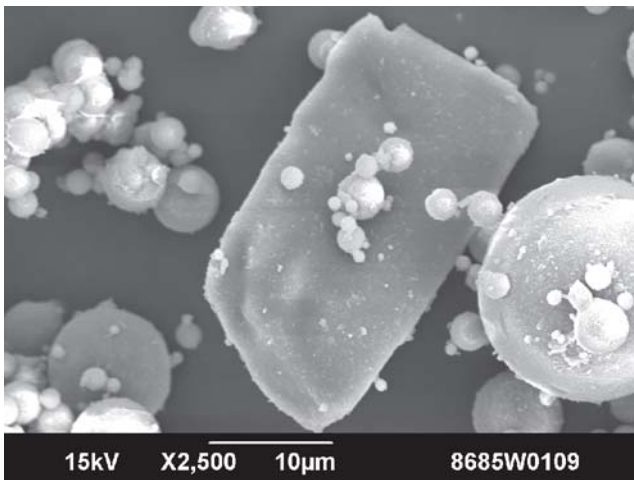


Figure 16. Smooth, non-spherical coal ash particle.

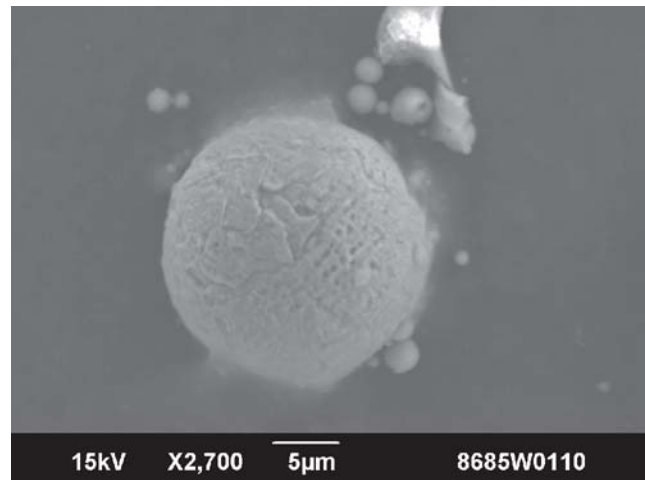


Figure 17. Bumpy coal ash sphere with iron deposits.

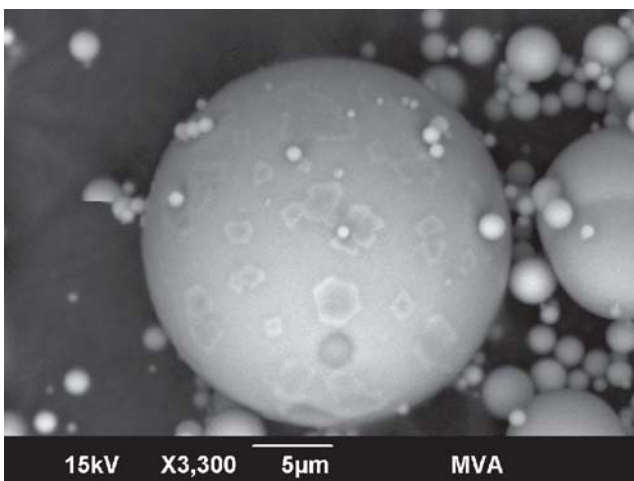


Figure 18. Etched coal ash sphere.

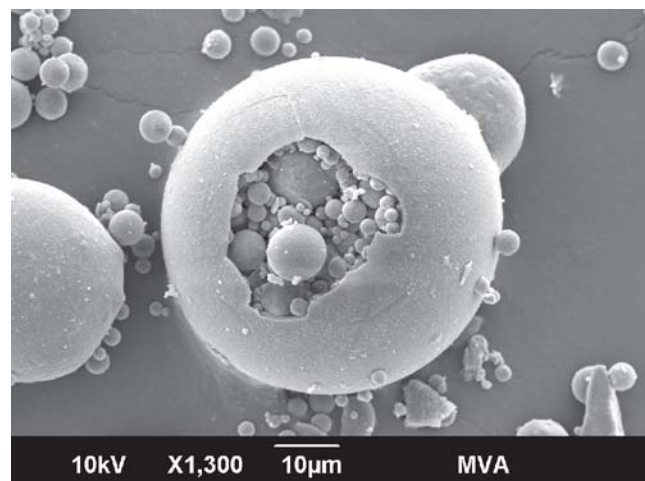


Figure 19. Plerosphere.

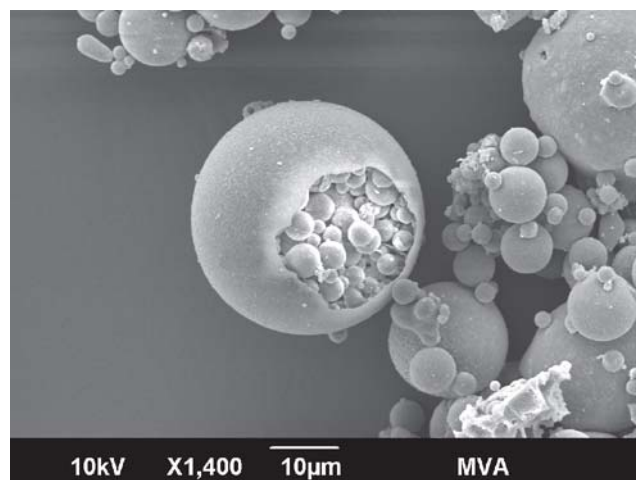


Figure 20. Plerosphere.

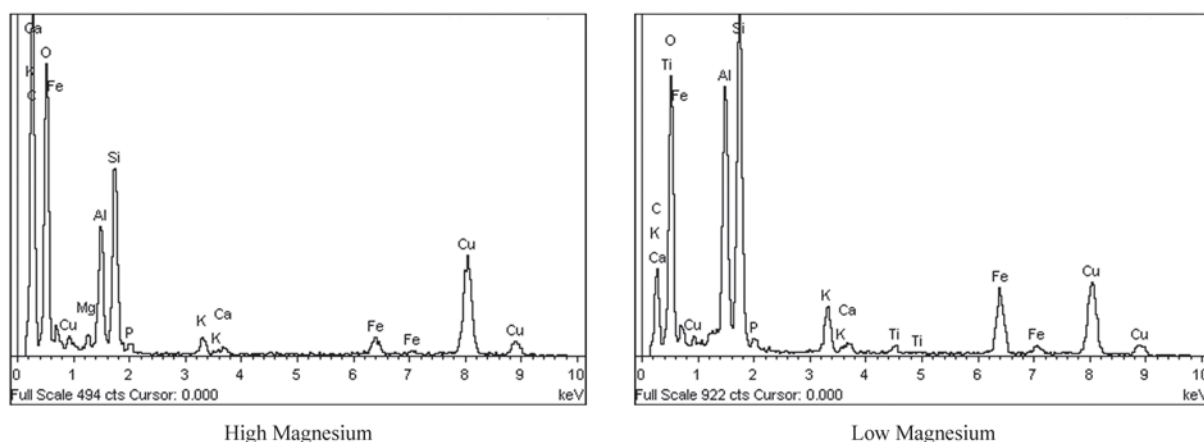


Figure 21. Range of fly ash composition determined in one sample by X-ray EDS: high and low magnesium.

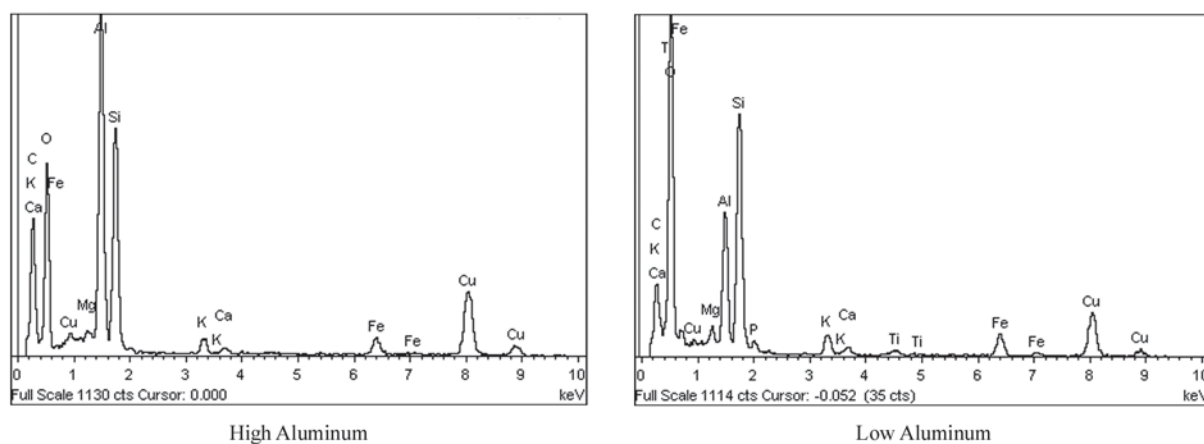


Figure 22. Range of fly ash composition determined in one sample by X-ray EDS: high and low aluminum.

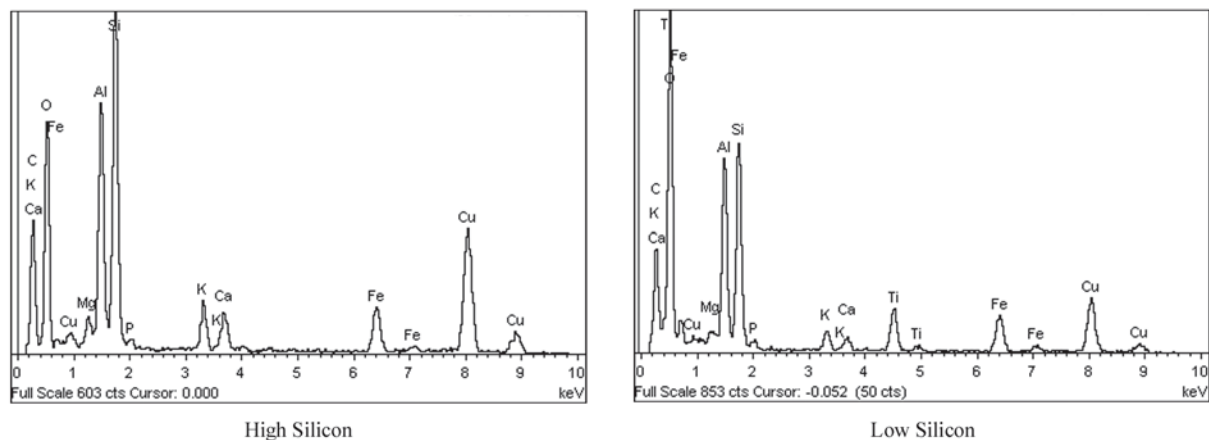


Figure 23. Range of fly ash composition determined in one sample by X-ray EDS: high and low silicon.

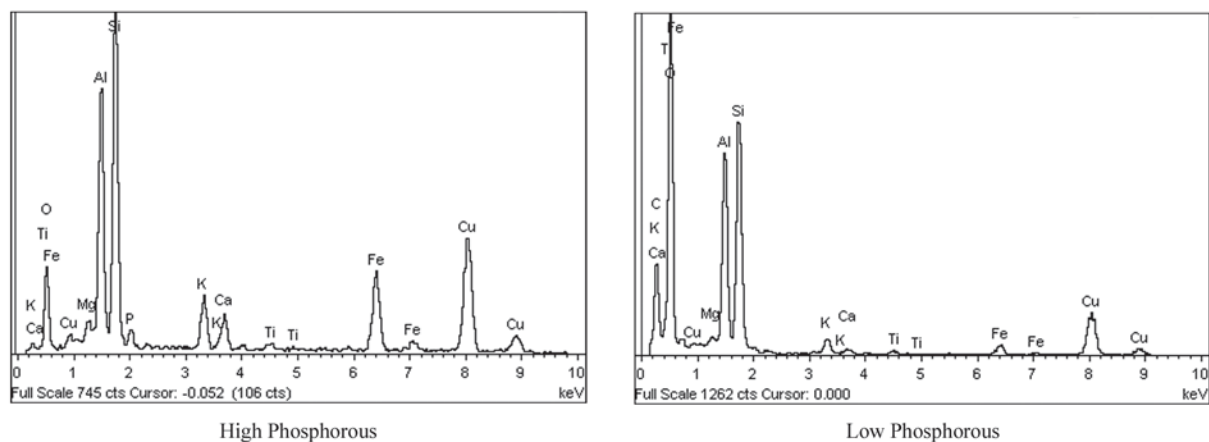


Figure 24. Range of fly ash composition determined in one sample by X-ray EDS: high and low phosphorous.

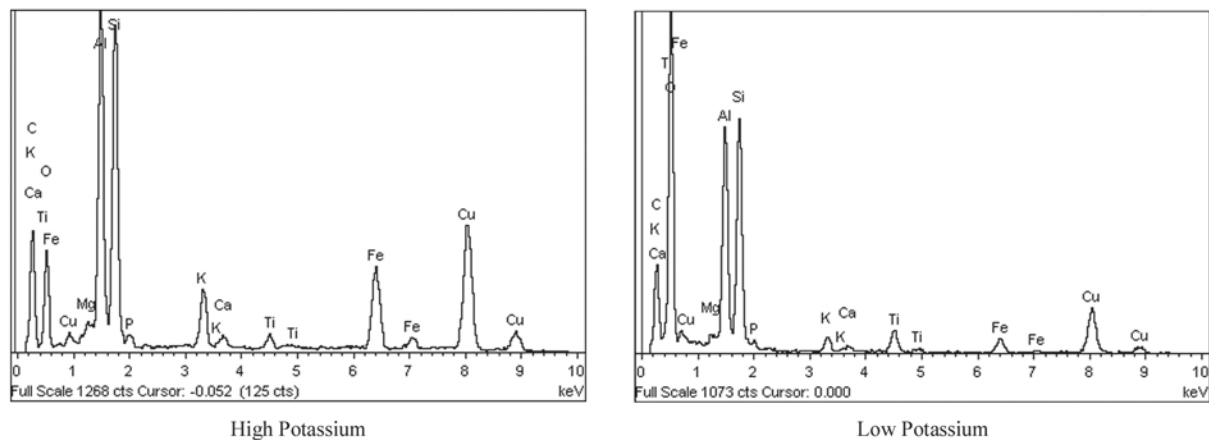


Figure 25. Range of fly ash composition determined in one sample by X-ray EDS: high and low potassium.

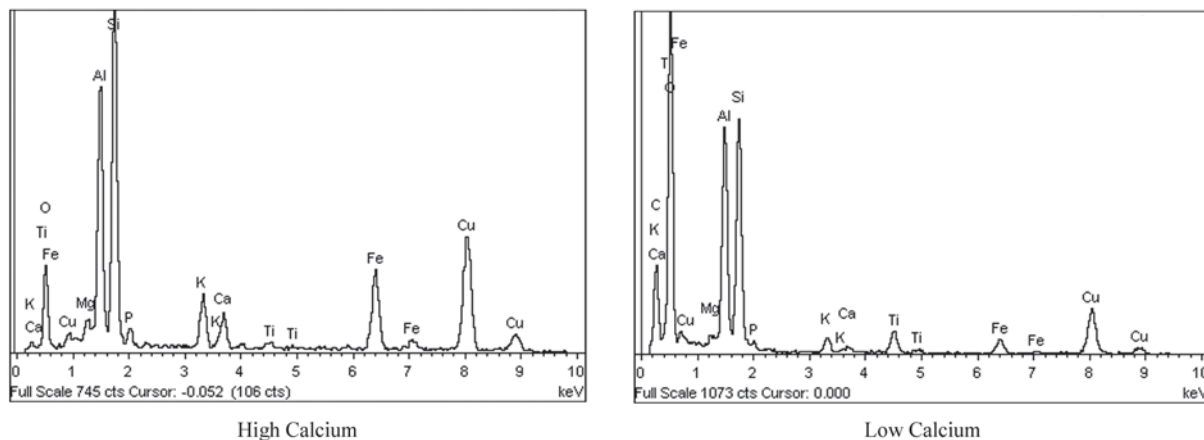


Figure 26. Range of fly ash composition determined in one sample by X-ray EDS: high and low calcium.

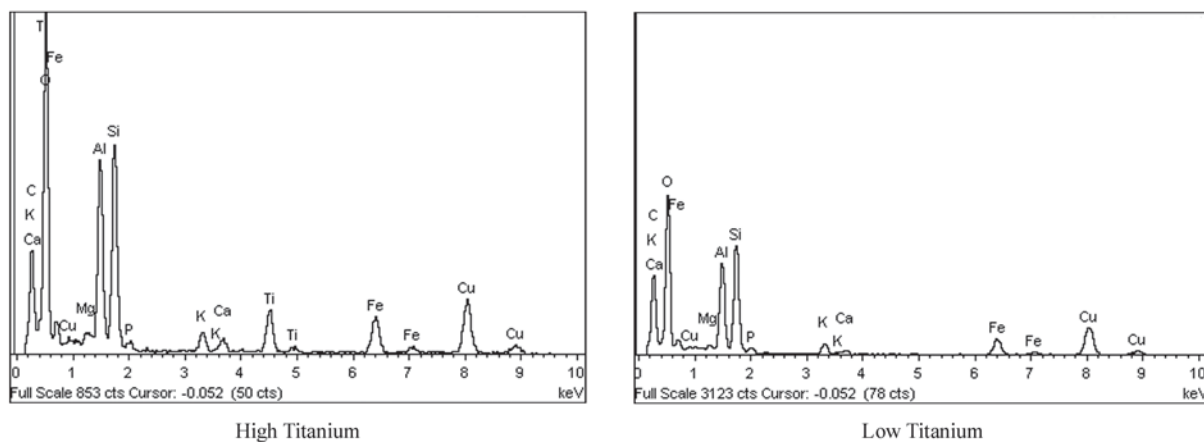


Figure 27. Range of fly ash composition determined in one sample by X-ray EDS: high and low titanium.

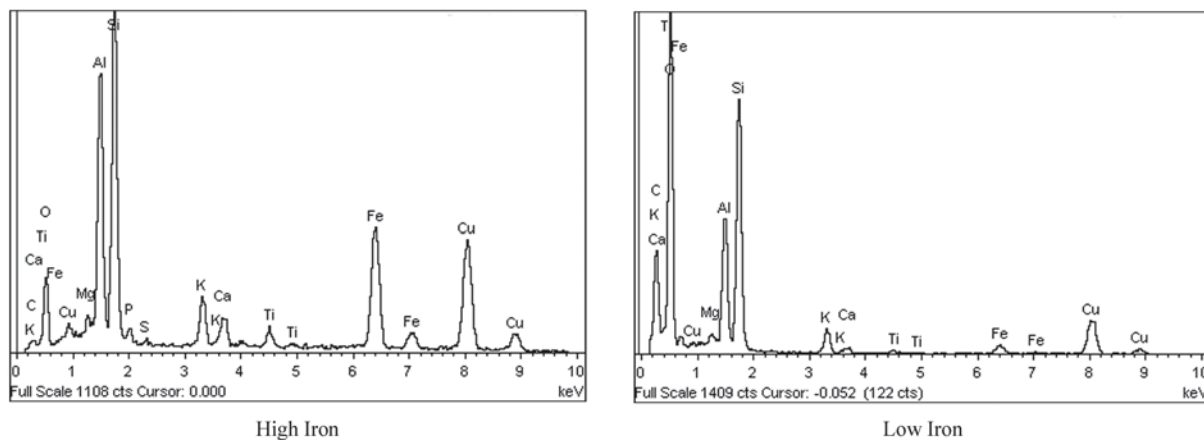
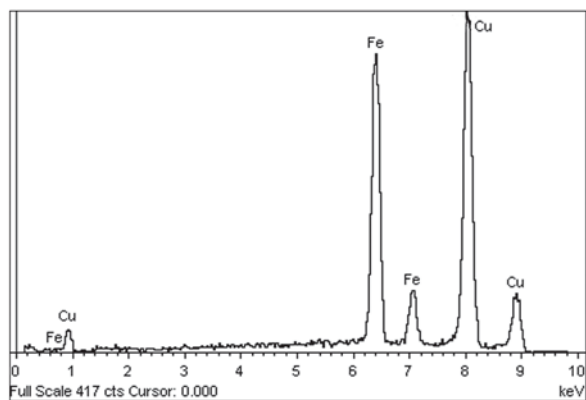
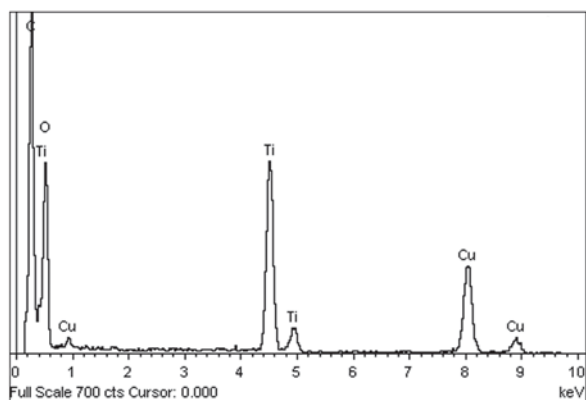


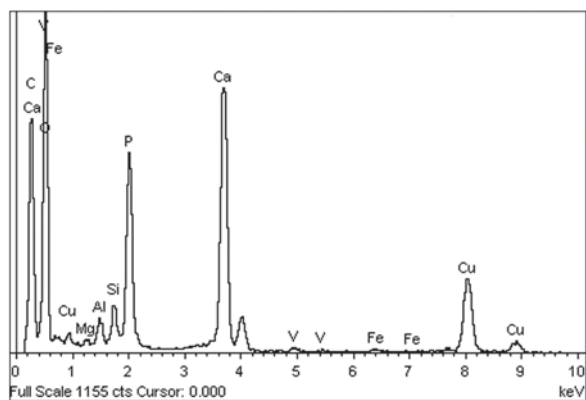
Figure 28. Range of fly ash composition determined in one sample by X-ray EDS: high and low iron.



Iron Sphere



Titanium Sphere



High Phosphorous and Calcium with Vanadium

Figure 29. Range of fly ash composition determined in one sample by X-ray EDS: iron sphere, titanium sphere, and high phosphorous and calcium with vanadium.