

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/215453673>

Mineralogy, Chemical Composition, and Microstructure of Ferrospheres in Fly Ashes from Coal Combustion

ARTICLE *in* ENERGY & FUELS · JULY 2006

Impact Factor: 2.79 · DOI: 10.1021/ef060008f

CITATIONS

37

READS

43

5 AUTHORS, INCLUDING:



Yongchun Zhao

Huazhong University of Science and Technol...

68 PUBLICATIONS 406 CITATIONS

SEE PROFILE

Mineralogy, Chemical Composition, and Microstructure of Ferrospheres in Fly Ashes from Coal Combustion

Yongchun Zhao,[†] Junying Zhang,^{*,†} Junmin Sun,[‡] Xiangfei Bai,[§] and Chuguang Zheng[†]

State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, China, Tsinghua University, Beijing 100084, China, and China Coal Research Institute, Beijing 100015, China

Received January 5, 2006. Revised Manuscript Received April 21, 2006

Fourteen samples of coal and ferrospheres, which were recovered by dry magnetic separation from fly ashes, were collected from five power plants in China. The mineralogy, chemical composition, and microstructure of ferrospheres in fly ashes have been studied by optical microscopy, X-ray diffraction (XRD), Mössbauer spectroscopy, and field emission scanning electron microscopy equipped with energy-dispersive X-ray spectroscopy (FSEM-EDX). Iron in ferrospheres mainly occurs as Fe_3O_4 , $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, MgFe_2O_4 , and Fe^{3+} -glass, ferrian spinel, and so on. On the basis of iron content, the ferrospheres in fly ashes are classified into four groups, namely ferrooxides ($\text{Fe} \geq 75\%$), aluminosilicate-bearing ferrooxides ($75\% > \text{Fe} \geq 50\%$), high-ferriiferous aluminosilicates ($50\% > \text{Fe} \geq 25\%$), and ferroaluminosilicates ($\text{Fe} < 25\%$). Ferrooxides are derived from the oxidation of iron-bearing minerals, whereas aluminosilicate-bearing ferrooxides, high-ferriiferous aluminosilicates, and ferroaluminosilicates are formed by the fusion of different proportions of inherent iron-bearing minerals and clay minerals. According to their microstructure, the ferrospheres in fly ashes are classified into seven groups, namely sheet ferrospheres, dendritic ferrospheres, granular ferrospheres, smooth ferrospheres, ferroplerospheres, porous ferrospheres, and molten drop ferrospheres. Sheet ferrospheres are derived from the oxidation of iron-bearing minerals immediately; smooth ferrospheres, molten drop ferrospheres, ferroplerospheres, and porous ferrospheres are the complex eutectic of inherent iron-bearing minerals and clay minerals; dendritic ferrospheres and granular ferrospheres are formed by the conglutination after the oxidation of iron-bearing minerals. Ferrooxides and aluminosilicate-bearing ferrooxides are important sources of the initial layer that occurs in deposits formed in coal-burning systems.

Introduction

Coal, which accounts for 75% of China's¹ and 36% of worldwide² electric power supply, has a series of industrial, technological, and environmental problems associated with its use. One of the most significant problems is slagging, the formation of molten deposits on the steam tubes during pulverized coal combustion. Mineral matter, especially iron-bearing minerals, has been recognized as a major source of fireside wall slagging in pulverized fuel boilers, which not only reduces the thermal efficiency of heat transfer of the exchanger surfaces but also affects their integrity as a result of corrosion and erosion.^{3–6}

Iron is the key variable in determining the slagging propensity on the basis of the following reasons: certain reducing forms

of iron, such as pyrrhotite, are self-sticking and can initiate the formation of slag deposits;^{3,7} at the same time, iron as Fe^{2+} can lower the melting point of aluminosilicate melts.⁸ In addition, iron in slag deposits, or in silicate melts, will increase the stickiness of these melts.^{3,7} Thus, it is important to have a better understanding of the transformation of iron-bearing minerals during coal combustion. Knowledge of the original mineral composition, chemical composition, and morphology of iron-bearing minerals in coal and fly ash can be helpful in interpreting the transformation process of iron-bearing minerals during coal combustion.

More than 316 and 188 minerals in coal and fly ash, respectively, have been identified, and most of them are accessory or trace minerals.^{9,10} XRD (X-ray diffraction) is a very useful technique and one of the most commonly and widely used methods for the identification and characterization of mineral matters in coal and fly ash.¹⁰ Mössbauer spectroscopy is one of the recommended methods for the investigation of fly

* To whom correspondence should be addressed. Tel: 86-27-87545526. Fax: 86-27-87545526. E-mail: jy Zhang@hust.edu.cn.

[†] State Key Laboratory of Coal Combustion.

[‡] Tsinghua University.

[§] China Coal Research Institute.

(1) *Strategic Research of Energy Development* (in Chinese); Chemical Industry Press: Beijing, 2004; pp 127.

(2) *International Energy Outlook 2000*; Energy Information Administration, Report#DOE/EIA-04842000; U.S. Department of Energy: Washington, DC, 2000.

(3) Raask, E. *Mineral Impurities in Coal Combustion: Behavior Problems and Remedial Measures*; Hemisphere Publishing: New York, 1985; pp 484.

(4) Aikin, T. L. H.; Cashion, J. D.; Ottrey, A. L. *Fuel* **1984**, *63*, 1269–1275.

(5) Cen, K. F.; Fan, J. R.; Chi, Z. H.; Shen L. C. *Prevention and Calculation of the Fouling, Slag, Abrasion and Erosion of the Boiler and Heat Exchanger* (in Chinese); Science Press: Beijing, 1994; pp 595.

(6) Bayers, R. W.; Walchuk, D. R. *Investigation of Pyrite as a Contributor to Slagging in Eastern Bituminous Coal*; Final Report, DOE Contract DE-AC22-81PC-40268; U.S. Department of Energy: Washington, DC, 1985.

(7) Adams, R. B.; Austin, L. G. *Fuel* **1985**, *64*, 832–838.

(8) Bool, L. E. I.; Peterson, T. W.; Wendt, J. O. *Combust. Flame* **1995**, *100*, 262–270.

(9) Finkelman, R. B. *Modes of Occurrence of Trace Elements in Coal*; U.S. Geological Survey Open-File Report, 81-99; U.S. Geological Survey, U.S. Department of the Interior: Reston, VA, 1981; p 322.

(10) Vassilev, S. V.; Vassileva, C. G. *Energy Fuels* **2005**, *19*, 1084–1098.

ashes enriched in iron, and particularly the magnetic and heavy fractions isolated from them.^{10–19} Iron-bearing minerals in coal and fly ash can also be investigated by scanning electron microscope and an electron microprobe technique.^{10,14} The characteristics of iron-bearing minerals in the coal and fly ash that were analyzed by Mössbauer spectroscopy, XRD, or similar techniques have been discussed broadly.^{10–26} Iron in coal is associated with sulfur pyrite (FeS₂), and non-sulfur-bearing minerals such as ankerite (CaFe(CO₃)₂), siderite (FeCO₃), and Fe²⁺-illite (clay mineral).^{11,16,19,24–28} Iron also occurs as an impurity element in other minerals, such as quartz, kaolinite, boehmite, rutile, and galena.^{9,28–39}

Iron-bearing minerals in fly ashes are derived mainly from the decomposition and oxidation of pyrite, siderite, and ankerite in feed coals during combustion process.^{4,6,7,13,15,17–19,24,28,30} Both dry and wet magnetic separations are effective procedures for isolating some iron-bearing minerals and phases from fly ashes.^{10,22,37,38,40–44} According to microprobe analysis and XRD as well as Mössbauer spectroscopy investigation, major iron-

bearing minerals in fly ashes are ferrispinel (79–90 wt %), represented by complex solid solutions based on magnetite with admixtures of Mg, Mn, and Ca; hematite; and maghemite.^{38,45,46} The morphology and chemical composition of ferrospheres in fly ashes from coal-fired power plants also have been conducted using optical microscope, FSEM-EDX (field emission scanning electron microscope equipped with energy-dispersive X-ray spectroscopy) and other similar techniques, which were summarized by many researchers.^{22,23,38,40,42–45,47–50} Light-microscopic morphologic appearances of individual coal fly ash particle are correlated with their elemental composition.^{50–51} And there are morphological differences in different size fractions of ferrospheres in fly ashes.⁴⁹ But there is still a lack of systematic interpretation of the morphology of ferrospheres in fly ashes, especially for the fly ash in China's power plants.

As a major source of furnace wall slagging, pyrite and other sulfide minerals (marcasite, pyrrhotite, etc.) in coal have been the focus of many studies, including Frankie et al. (1987), Querol et al. (1989), Hower and Pollock (1989), Renton and Bird (1991), Kortenski and Kostova (1996), and so on.^{52–56} The transformations of iron-bearing minerals during coal combustion have also been discussed.^{5,8,19,24,57–65} Most of these studies focus on the transformation process, with little information about the characteristic of ferrospheres.

As a sequel of previous studies, the present paper reports the results of extended investigations on the characteristics of iron-bearing minerals and the chemical composition and morphology

(11) Ahmed, M. A.; Vandenbergh, R. E.; Grave, E. D.; Eissa, N. A.; Ibarra, J. V. *Fuel* **1999**, 78, 453–457.

(12) Montano, P. A. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **1979**, 2.

(13) Verma, H. C.; Tripathi, R. P. *Fuel* **2000**, 79, 599–606.

(14) Huggins, F. E.; Huffman, G. P.; Lee, R. J. Scanning Electron Microscope-Based Automated Image Analysis (SEM-AIA) and Mössbauer Spectroscopy: Quantitative Characterization of Coal Minerals. In *Coal and Coal Products: Analytical Characterization Techniques*; Fuller, E. F., Jr., Ed.; ACS Symposium Series 205; American Chemical Society: Washington, DC, 1982; pp 239–258.

(15) Taneja, S. P.; Jones, C. H. W. *Fuel* **1984**, 63, 695–701.

(16) Tripathi, P. S. M.; Ram, L. C.; Rao, S. K. *Erdoel Kohle, Erdgas, Petrochem.* **1986**, 470–471.

(17) Dai, S. F.; Chou, C. L.; Yue, M.; Luo, K. L.; Ren, D. Y. *Int. J. Coal Geol.* **2005**, 61, 241–258.

(18) Michael, P. J.; Monsef-Mirzai, P.; McWhinnie, W. R. *Fuel* **1991**, 70, 119–121.

(19) Ram, L. C.; Tripathi, P. S.; Mishra, S. P. *Fuel Process. Technol.* **1995**, 42, 47–60.

(20) Pankhurst, Q. A.; McCann, V. H.; Newman, N. A. *Fuel* **1986**, 65, 880–883.

(21) Huffman, G. P.; Huggins, F. E. Analysis of the Inorganic Constituents in Low-Rank Coals. In *Chemistry of Low-Rank Coals*; Schobert, H. H., Ed.; ACS Symposium Series 264; American Chemical Society: Washington, DC, 1984; pp 159–174.

(22) Vassilev, S. V.; Vassileva, C. G.; Karayigit, A. I.; Bulut, Y.; Alastuey, A.; Querol, X. *Int. J. Coal Geol.* **2005**, 61, 65–85.

(23) Vassilev, S. V.; Vassileva, C. G.; Karayigit, A. I.; Bulut, Y.; Alastuey, A.; Querol, X. *Int. J. Coal Geol.* **2005**, 61, 35–63.

(24) McLennan, A. R.; Bryant, G. W.; Bailey, C. W.; Stanmore, B. R.; Wall, T. F. *Energy Fuels* **2000**, 14, 308–315.

(25) Zhang, J.; Ren, D.; Zhu, Y.; Chou, C.; Zeng, R.; Zheng, B. *Int. J. Coal Geol.* **2004**, 57, 49–61.

(26) Zhang, J.; Ren, D.; Zheng, C.; Zeng, R.; Chou, C.; Liu, J. *Int. J. Coal Geol.* **2002**, 53, 55–64.

(27) Clark, T. M.; Evans, B. J.; Wynter, C.; Pollak, H. *Hyperfine Interact.* **1998**, 112, 227–230.

(28) Waanders, F. B.; Vinken, E.; Mans, A.; Mulaba-Bafubandi, A. F. *Hyperfine Interact.* **2003**, 148, 21–29.

(29) Dai, S. F.; Li, D. H.; Ren, D. Y.; Tang, Y. G.; Shao, L. Y.; Song, H. B. *Appl. Geochem.* **2004**, 19, 1315–1330.

(30) Vassilev, S. V.; Vassileva, C. G. *Fuel Process. Technol.* **1996**, 48, 85–106.

(31) Ward, C. R. *Int. J. Coal Geol.* **2002**, 50, 169–214.

(32) Ward, C. R.; Taylor, J. C. *Int. J. Coal Geol.* **1996**, 30, 211–229.

(33) Finkelman, R. B.; Bostick, N. H.; Dulong, F. T.; Senftle, F. E.; Thorpe, A. N. *Int. J. Coal Geol.* **1998**, 36, 223–241.

(34) Gupta, R. P.; Wall, T. F.; Kajigaya, I.; Miyamae, S.; Tsumita, Y. *Prog. Energy Combust. Sci.* **1998**, 24, 523–543.

(35) Hower, J. C.; Mastalerz, M. *Energy Fuels* **2001**, 15, 1319–1321.

(36) Patterson, J. H.; Corcoran, J. F.; Kinealy, K. M. *Fuel* **1994**, 73, 1735–1745.

(37) Hower, J. C.; Rathbone, R. F.; Robertson, J. D.; Peterson, G.; Trimble, A. S. *Fuel* **1999**, 78, 197–203.

(38) Sokol, E. V.; Kalugin, V. M.; Nigmatulina, E. N.; Volkova, N. I.; Frenkel, A. E.; Maksimova, N. V. *Fuel* **2002**, 81, 867–876.

(39) Zdrov, E. L.; Cleal, C. J. *Int. J. Coal Geol.* **1999**, 41, 371–393.

(40) Vassilev, S. V.; Menendez, R.; Diaz-Somoano, M.; Martinez-Tarazona, M. R. *Fuel* **2004**, 83, 585–603.

(41) Fisher, G.; Natusch, D. Size Dependence of the Physical and Chemical Properties of Coal Fly Ash. In *Analytical Methods for Coal and Coal Products*; Karr, J. C., Ed.; Academic Press: New York, 1979; Vol. 3, pp 489.

(42) Norton, G. A.; Markuszewski, R.; Shanks, H. R. *Environ. Sci. Technol.* **1986**, 20, 409–413.

(43) Vassilev, S. V.; Menendez, R.; Borrego, A. G.; Diaz-Somoano, M.; Martinez-Tarazona, M. R. *Fuel* **2004**, 83, 1563–1583.

(44) Vassilev, S. V.; Vassileva, C. G. *Fuel Process. Technol.* **1996**, 47, 261–280.

(45) Fomenko, E. V.; Kondratenko, E. V.; Salanov, A. N.; Bajukov, O. A.; Talysh, A. A.; Maksimov, N. G.; Nizov, V. A.; Anshits, A. G. *Catal. Today* **1998**, 42, 267–272.

(46) Femenko, E. V. Magnetic Microspheres of Constant Composition and Their Catalytic Properties in Reactions of Methane Oxidative Transformation. Ph.D. Thesis, Russian Academy of Sciences, Krasnoyarsk, Russia, 1998.

(47) Sokol, E. V.; Maksimova, N. V.; Volkova, N. I.; Nigmatulina, E. N.; Frenkel, A. E. *Fuel Process. Technol.* **2000**, 67, 35–52.

(48) Fisher, G.; Chang, D.; Brummer, M. *Science* **1976**, 192, 553–555.

(49) Das, S. K. *Indian Concr. J.* **2003**, 77, 1300–1303.

(50) Anshits, A. G.; Kondratenko, E. V.; Fomenko, E. V.; Kovalev, A. M.; Anshits, N. N.; Bajukov, O. A.; Sokol, E. V.; Salanov, A. N. *Catal. Today* **2001**, 64, 59–67.

(51) Prentice, B. A.; Fisher, G. L.; Lai, C. E.; Hayes, T. L. *Aerosol Sci. Technol.* **1983**, 2, 252–257.

(52) Frankie, K. A.; Hower, J. C. *Int. J. Coal Geol.* **1987**, 7, 349–364.

(53) Querol, X.; Chinchon, S.; Lopez-Soler, A. *Int. J. Coal Geol.* **1989**, 11, 171–189.

(54) Hower, J. C.; Pollock, J. D. *Int. J. Coal Geol.* **1989**, 11, 227–245.

(55) Kortenski, J.; Kostova, I. *Int. J. Coal Geol.* **1996**, 29, 273–290.

(56) Renton, J. J.; Bird, D. S. *Int. J. Coal Geol.* **1991**, 17, 21–50.

(57) Srinivasachar, S.; Helble, J. J.; Boni, A. A. *Prog. Energy Combust. Sci.* **1990**, 16, 281–292.

(58) Helble, J. J.; Srinivasachar, S.; Boni, A. A. *Prog. Energy Combust. Sci.* **1990**, 16, 267–279.

(59) Srinivasachar, S.; Helble, J. J.; Boni, A. A.; Shah, N.; Huffman, G. P.; Huggins, F. E. *Prog. Energy Combust. Sci.* **1990**, 16, 293–302.

(60) Srinivasachar, S.; Boni, A. A. *Fuel* **1989**, 68, 829–836.

(61) Huffman, G. P.; Huggins, F. E.; Levasseur, A. A.; Chow, O.; Srinivasachar, S.; Mehta, A. K. *Fuel* **1989**, 68, 485–490.

(62) Baxter, L. L.; Mitchell, R. E. *Combust. Flame* **1992**, 88, 1–14.

(63) Baxter, L. L. *Combust. Flame* **1992**, 90, 174–184.

(64) Grovest, S. J.; Williamson, J.; Sanyal, A. *Fuel* **1987**, 66, 461–466.

(65) Yan, L.; Gupta, R.; Wall, T. *Energy Fuels* **2001**, 15, 389–394.

Table 1. Iron-Bearing Minerals in Coals^a

category	mineral	chemical formula
sulfides	pyrite	FeS ₂
	marcasite	FeS ₂
	greigite	Fe ₃ S ₄
	pyrrhotite	Fe _{1-x} S
	arsenopyrite	FeAsS
	chalcopyrite	CuFeS ₂
	bornite	Cu ₅ FeS ₃
	tetrahedrite	(Cu,Fe ₁₂)Sb ₄ S ₁₃
	bravoite	(Ni, Fe)S ₂
	siderite	FeCO ₃
carbonates	ferrodolomite	Ca(Fe, Mg)[CO ₃] ₂
	ankerite	Ca(Fe, Mg)[CO ₃] ₂
silicates	illite	K _{0.75} (Al _{1.75} R _{0.25} ²⁺)(Si _{3.50} Al _{0.50})O ₁₀ (OH) ₂ (R = Fe, Mg, Ti)
	chlorite	(Mg,Fe,Al) ₆ [(Si,Al) ₄ O ₁₀][OH] ₈
	clinochlore	(Mg,Fe) _{4.75} Al _{1.25} [Al _{1.25} Si _{2.75} O ₁₀](OH) ₈
	allanite	(Ca, Ce) ₂ (Fe ³⁺ , Fe ²⁺)Al ₂ [SiO ₄][Si ₂ O ₇]O(OH)
	actinolite	Na ₂ Ca ₄ (Mg,Fe) ₁₀ [Si ₄ O ₁₁] ₄ O ₂ [OH] ₂
	amphibole	Ca ₂ Fe ₂ Al ₂ Si ₂ O ₄
	gadolinite	Y ₂ FeBe ₂ [SiO ₄] ₂ O ₂
	tourmaline(dravite)	Na(Mg,Fe,Mn) ₃ Al ₆ B ₃ Si ₆ O ₂₇ (OH) ₄
	biotite	K(Mg,Fe) ₃ [AlSi ₃ O ₁₀](OH,F) ₂
	ferrihalloysite	CaNa(Mg,Fe)(Al,Fe,Ti)SiO(OH,F),
sulfates	hornblende	(Fe ²⁺ , Mg, Mn) ₂ (Al, Fe ³⁺)Al ₃ O ₂ [SiO ₄](OH) ₄
	chloritoid	
	szomolnokite	FeSO ₄ ·H ₂ O
	rozenite	FeSO ₄ ·4H ₂ O
	ferroalumen	FeSO ₄ ·5H ₂ O
	melanterite	FeSO ₄ ·7H ₂ O
	jarosite	KFe ₃ [SO ₄] ₂ (OH) ₆
	natrojarosite	NaFe ₃ [SO ₄] ₂ (OH) ₆
	coquimbite	Fe ₂ [SO ₄] ₃ ·9H ₂ O
	halotrichite	FeAl ₂ [SO ₄] ₄ ·22H ₂ O
oxides and hydroxides	roemerite	FeFe ₂ ³⁺ [SO ₄] ₄ ·6H ₂ O
	sideronatrite	Na ₂ Fe[SO ₄](OH)·3H ₂ O
	hematite	Fe ₂ O ₃
	maghemite	Fe ₂ O ₃
	magnetite	Fe ₃ O ₄
	goethite	FeOOH
	lepidocrocite	Fe ₂ O ₃ ·H ₂ O
	limonite	HFeO ₂ ·nH ₂ O
	magnesioferrite	MgFe ₂ O ₄
	calcium ferrite	CaFe ₂ O ₄
others (rarely occur in coals)	srebrodolskite	Ca ₂ Fe ₂ O ₅
	brownmillerite	Ca ₄ Al ₂ Fe ₂ O ₁₀
	columbite	(Fe, Mn)Nb ₂ O ₆
	ilmenite	FeTiO ₃
	chromite	FeCr ₂ O ₄
	spinel	(Me, Fe, Zn, Mn)(Al, Cr, Fe) ₂ O ₄ (Me = metal elements)

^a Compiled from various sources.

of ferrospheres in the fly ashes from pulverized coal-fired power plants in China.

Samples and Analytical Procedures

Samples. The coal samples used for this study were collected from several major coalfields (Junger, Yanzhou, Qianxi, Shenfu, Datong, Jiaozuo, Xiaolongtan, and Changcun) in China. The fly ash samples were collected from the hoppers of electrostatic precipitators of five pulverized coal-fired power plants (Qingshan, Ezhou, Jiaozuo, Yaomeng, and Xiaolongtan) in China. The ferrospheres were recovered by dry magnetic separation (with a hand magnet) from the fly ashes.

Analytical Techniques. An optical microscope was used for mineral and maceral observations under reflected light. Major and minor minerals in coal and fly ashes were identified using XRD. XRD studies were carried out on an χ 'Pert PRO diffractometer equipped with a graphite diffracted-beam monochromator. The accelerating voltage was 40 kV and the current was 40 mA. Diffraction patterns were collected at 5–70° 2 θ using Cu K α radiation. The iron-bearing minerals were also identified using a WISSEL Mössbauer spectrometer. The Mössbauer spectrum of each ferrosphere was separately recorded at 25 °C. The absorbers were

prepared by pressing the powder in a copper ring and fixing the open ends with cellophane tapes. A constant acceleration Mössbauer spectrometer was used with a ⁵⁷Co source in the rhodium matrix. Spectral Mössbauer parameters were determined by fitting sets of Lorentzian lines to the experimental data using the standard least-squares minimization technique. The investigations by FSEM (field emission scanning electron microscopy) were carried out on a Sirion200 microscope equipped with a GENESIS EDX (energy-dispersive X-ray spectroscopy). FSEM-EDX was used to study the morphology and composition of ferrospheres.

Results and Discussion

Iron-Bearing Minerals in Coal. The iron-bearing minerals found in coal are listed in Table 1 (compiled from various sources^{3–6,8–9,11–23,25–34,36,39,44,53,55–56,66,67}). The categories of iron-bearing minerals include sulfides (mainly pyrite and marcasite), carbonates (such as siderite) and oxides, a minor

(66) Swaine, D. J. *Trace Elements in Coal*; Butterworths: London, 1990; p 294.

(67) Lored, J.; Alvarez, R.; Ordóñez, A. *Sci. Total Environ.* **2005**, *340*, 247–260.

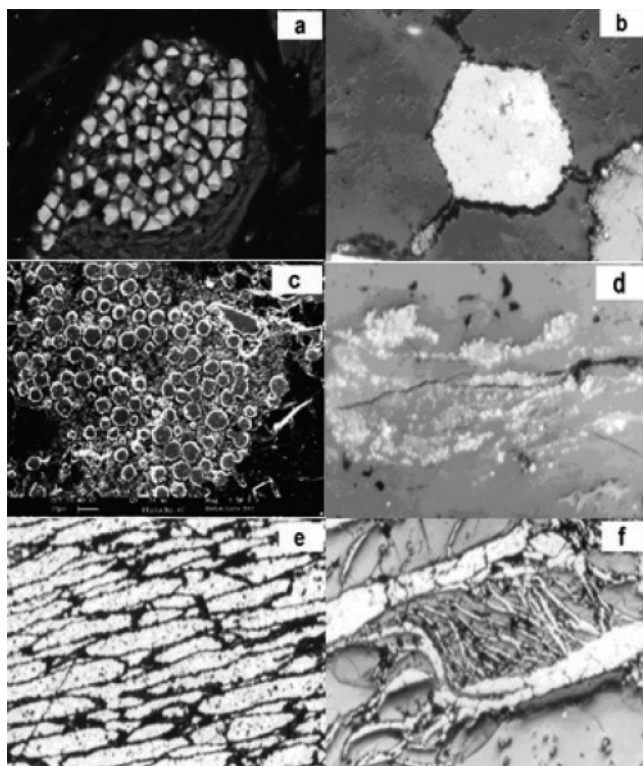


Figure 1. Photomicrographs of pyrite in coals: (a) discrete crystal particles in the Yanzhou coal, backscattering image, 4000 \times ; (b) euhedral crystals in the Qinglonggaoling coal, Qianxi, reflected light, 300 \times , P2; (c) framboids in the Puannibao coal, Qianxi, SEM, 1500 \times , P2; (d) colloform pyrite in the Puanlouxia coal, Qianxi, reflected light, 200 \times , P2; (e) pyrite occurring as cell- and cavity-infillings in the Zhenfenwanlan coal, Qianxi, reflected light, 100 \times , T3; (f) pyrite vein in the Qinglonggaoling coal, Qianxi, reflected light, 50 \times , P2.

amount of silicates, and some rare sulfates, hydroxides, and others, as presented in Table 1.

Sulfides are typical authigenic minerals in coal.³⁰ Pyrite occurs in various forms in coal,^{55,68–70} for example, as individual and clustered euhedral crystals (Figure 1b), isolated anhedral, and massive but internally crystalline accumulations, framboid (Figure 1c), colloform (Figure 1d), nodules, lens-shaped masses, in cleats (Figure 1f) and fractures, or as discrete particles (Figure 1a) in veinlets. Pyrite may also occur as a cell- or cavity-infilling (Figure 1e), or as replacement of the maceral components. Special terms, such as “specular pyrite”⁵⁴ and “fibrous pyrite”,⁵³ are also used to describe particular modes of pyrite occurrence. Marcasite often occurs in low-rank coal. The distinction between pyrite and marcasite is conducted easily by polarizing microscopy under reflected light (Figure 2). The marcasite with heterogeneous and parallel twin structure is obviously different from pyrite, and often shows a taupe-celandine green interference color. The formation of pyrite or marcasite is probably related to pH variations in the micro-environment during peat accumulation.⁵³ Various accessory iron-bearing sulfides such as chalcopyrite (Figure 3), arsenopyrite, bravoite, and getchellite may also occur in the coals studied,^{67,71–72} but they almost have

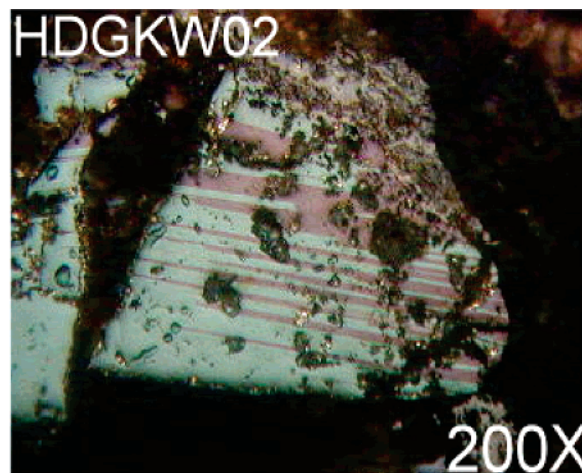


Figure 2. Optical photomicrograph of marcasite crystals in the Heidaigou coal, Junger, polarizing reflected light, 200 \times .

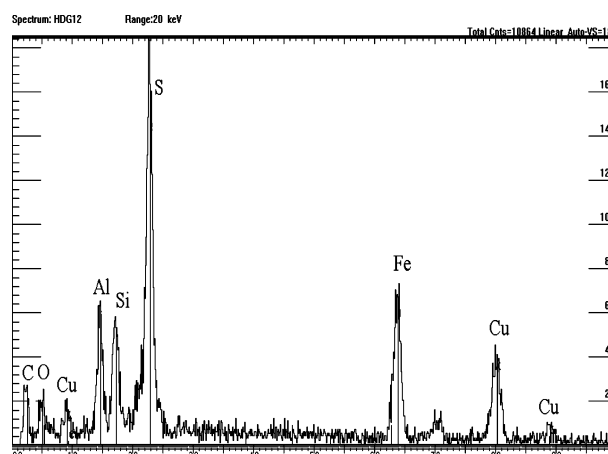


Figure 3. Energy-dispersive X-ray spectrum of Fe in chalcopyrite from the Heidaigou coal, Junger.

no impact on the formation of deposits and slagging because of their little content. Sulfides are the dominant Fe-bearing minerals in coal, and particularly, pyrite has been considered as a major contribution of furnace wall slagging.⁷³

Iron-bearing carbonates, including siderite and ankerite, often occur as discrete particles in coal. The behavior of siderite during coal combustion is relatively simple. However, siderite in a burning coal particle which contains clay minerals and/or quartz is likely to react with these minerals to form an aluminosilicate slag droplet.²⁴

Iron-bearing silicates are mainly clay minerals, such as illite and chlorite. Moreover, iron sometimes occurs as an impurity in these minerals. Illite is a common iron-bearing mineral in coal (Figure 4), especially in bituminous coal. Thus, the study of iron-bearing clay minerals has mainly focused on illite hitherto.⁵⁹ Silicate minerals are mainly of detrital terrigenous origin, and most of them are from weathering products of various sediment source regions.⁷⁴

Sulfate minerals in coals are weathering products of pyrite or marcasite.²⁸ Such as jarosite which is made up of prismatic and wedge-shaped crystals, often occurs as colloform crust and aggregates.^{13,30} While both iron oxides and oxyhydroxides in coal are weathering products of sulfide minerals. Besides some

(68) Dai, S.; Ren, D.; Tang, Y.; Shao, L.; Li, S. *Int. J. Coal Geol.* **2002**, 51, 237–250.

(69) Dai, S.; Hou, X.; Ren, D.; Tang, Y. *Int. J. Coal Geol.* **2003**, 55, 139–150.

(70) Dai, S.; Ai, T.; Jiao, F.; Ma, F.; Li, B. *Acta Petrol. Sin.* **2000**, 16, 269–274.

(71) Mao, J.; Lehmann, B.; Du, A.; Zhang, G.; Ma, D.; Wang, Y.; Zeng, M.; Kerrich, R. *Econ. Geol.* **2002**, 97, 1051–1061.

(72) Dai, S.; Zeng, R.; Sun, Y. *Int. J. Coal Geol.* **2006**, 66, 217–226.

(73) Couch, G. *Understanding Slagging and Fouling in pf Combustion*. IEA Coal Research: London, 1994.

(74) Dai, S.; Chou, C.; Yue, M.; Luo, K.; Ren, D. *Int. J. Coal Geol.* **2005**, 61, 241–258.

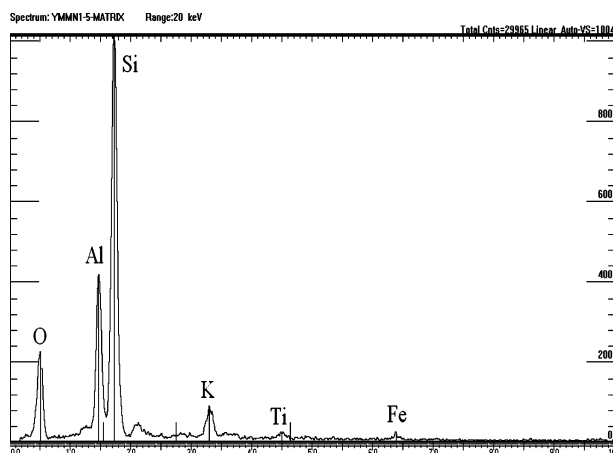


Figure 4. Energy-dispersive X-ray spectrum of Fe in illite from the Shendong coal, Shenfu.

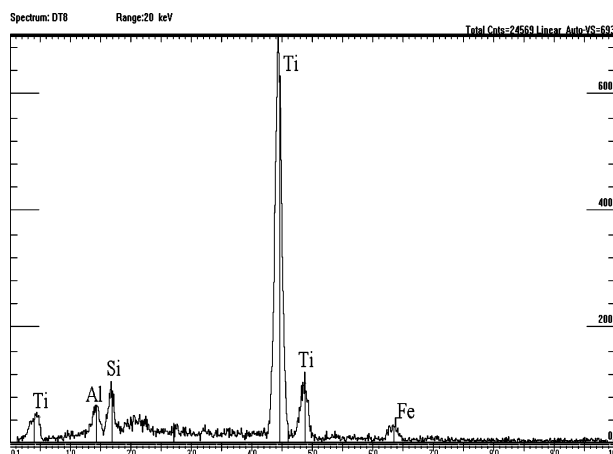


Figure 5. Energy-dispersive X-ray spectrum of Fe in rutile from the Datong coal.

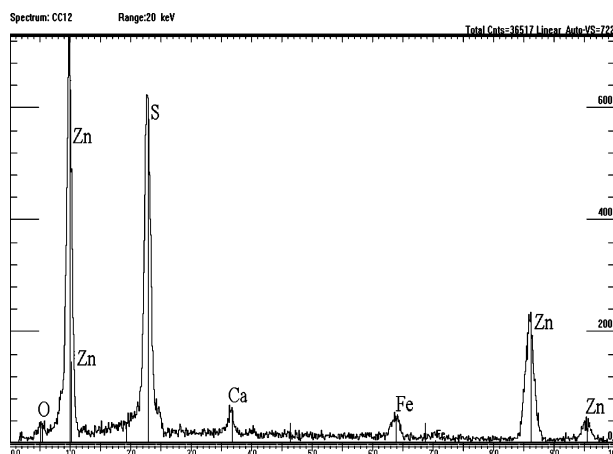


Figure 6. Energy-dispersive X-ray spectrum of Fe in sphalerite from the Changcun coal.

oxidation products may be formed during the storage and handling of coal.³⁰

In addition, there are many minerals containing a minor amount of iron as an impurity, such as rutile, sphalerite, svanbergite, apatite, polyhalite, barite, gypsum, anatase, and dolomite.^{29,31} Rutile is a common but minor mineral in coal, often containing Fe as an impurity (Figure 5). A trace amount of Fe in sphalerite is identified in the Changcun coal (Figure 6). These accessory sulfide minerals often occur as discrete particles dispersed in clay minerals or carbonate minerals.⁹

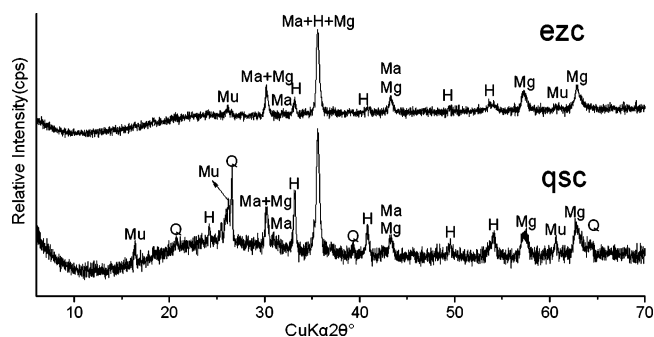


Figure 7. XRD patterns of ferrospheres separated from fly ashes (ezc: Ezhou power plant; qsc: Qingshan power plant) Mineral abbreviations: H, hematite; Ma, magnetite; Mg, magnesioferite; Mu, mullite; Q, quartz.

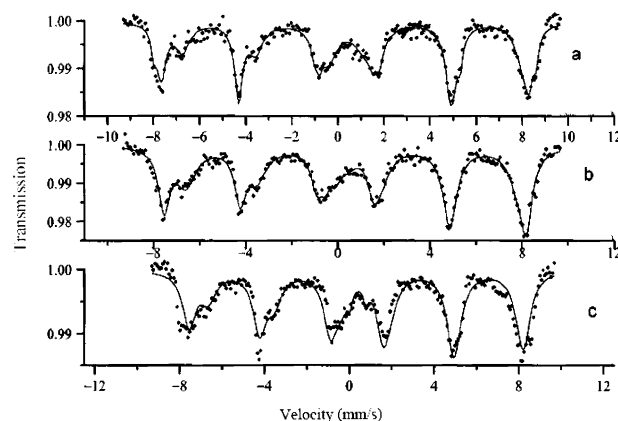


Figure 8. Mössbauer spectroscopic analysis of ferrospheres in fly ash from three power plants: (a) Jiaozuo, (b) Yaomeng, and (c) Xiaolongtan.

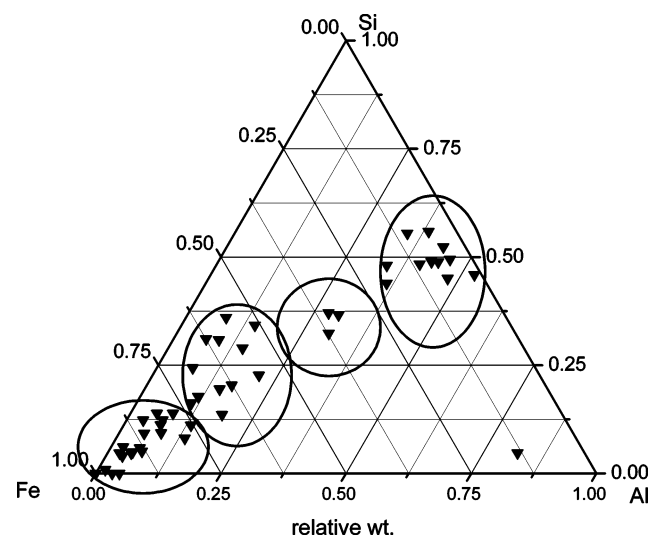


Figure 9. Ternary Fe-Si-Al diagram derived from FSEM-EDX data for ferrospheres.

Iron-Bearing Minerals in Fly Ash. The magnetic fractions in fly ashes from coal-fired power plants mainly include ferro-, ferri- and paramagnetic Fe-bearing minerals and phases.^{15,18,22,37,38,43,75} The ferrospheres separated from fly ash normally account for 0.5–18.1%.⁴³ A large percentage of ferrospheres are commonly 3–20 μm in size (Figure 10a). Table 2 presents the common minerals and phases, which are compiled from various sources.^{3,4,8,10,13,15,17–19,22,30,31,35,37,38,43,44,75,76} The

(75) Veranth, J. M.; Smith, K. R.; Huggins, F. E.; Hu, A. A.; Lighty, J. S.; Aust, A. E. *Chem. Res. Toxicol.* **2000**, *13*, 161–164.

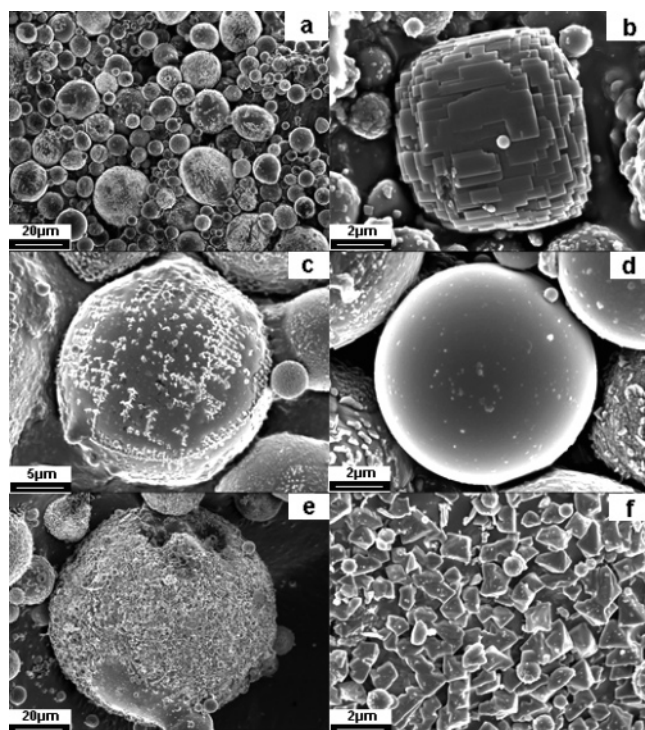


Figure 10. SEM images of ferrospheres (secondary electrons): (a) general view of ferrospheres; (b) sheet hematite in ferrospheres; (c) dendritic magnetite in ferrospheres; (d) smooth aluminosilicate ferrosphere; (e) granular ferrospheres coated with ferrian spinel; and (f) ferrian spinel enriched on the surface of ferrospheres.

Table 2. Iron-Bearing Minerals in Fly Ash^a

category	mineral	chemical formula
sulfides	pyrrhotite	Fe _{1-x} S
carbonates	ankerite	Ca(MgFe)(CO ₃) ₂
silicates	Ca-Fe silicate	
	chlorite	(Mg,Fe,Al) ₆ (Si,Al) ₄ O ₁₀ [OH] ₈
	biotite	K(Mg,Fe) ₃ [AlSi ₃ O ₁₀](OH,F) ₂
	Ca-Fe aluminosilicate	
	Fe-Mg aluminosilicate	
sulfates	Ca-Fe-Mg aluminosilicate	
	jarosite	KFe ₃ (SO ₄) ₂ (OH) ₆
	szomolnokite	FeSO ₄ ·H ₂ O
	rozenite	FeSO ₄ ·4H ₂ O
oxides	coquimbite	Fe ₂ [SO ₄] ₃ ·9H ₂ O
	wuestite	FeO
	hematite	Fe ₂ O ₃
	maghemite	Fe ₂ O ₃
	magnetite	Fe ₃ O ₄
	magnesioferrite	MgFe ₂ O ₄
	ferrian spinel	Mg(AlFe) ₂ O ₄
	calcium ferrite	CaFe ₂ O ₄
	srebrodolskite	Ca ₂ Fe ₂ O ₅
	ilmenite	FeTiO ₃
	jacobsite	MnFe ₂ O ₄
	hercynite	FeAl ₂ O ₄
	ulvospinel	TiFe ₂ O ₄
	brownmillerite	Ca ₄ Al ₂ Fe ₂ O ₁₀
	chromite	FeCr ₂ O ₄
	goethite	FeOOH
	lepidocrocite	FeOOH
	spinel	(Me,Fe,Zn,Mn)(Al,Cr,Fe) ₂ O ₄
	chromspinel	CrFe ₂ O ₄

^a Compiled from various sources.

proportion of Fe sulfides in fly ash obviously decreases because of the oxidation to Fe oxide sulfates and oxyhydroxides. The iron-bearing silicates in fly ash are formed by the fusion of different proportions of iron-bearing minerals and clay minerals. It appears that some proportion of Fe³⁺ sulfates (jarosite) in fly

Table 3. Mössbauer Parameters of Ferrospheres in Fly Ash from Three Power Plants^a

samples	iron speciation	δ^b (mm s ⁻¹)	Δ^b (mm s ⁻¹)	H (KOe)	relative area (%)
Jiaozuo	Fe ₃ O ₄	0.2962	-0.0315	477.26	37.33
		0.5762	0.0056	443.88	45.98
	α -Fe ₂ O ₃	0.3713	-0.1699	502.47	6.43
		0.5892	2.2128		3.72
Yaomeng	Fe ³⁺ -silicate	0.3891	0.8489		6.54
	Fe ₃ O ₄	0.2961	-0.0200	466.00	26.40
		0.5305	0.1000	444.00	36.50
	Fe ₂ O ₃	0.3024	0.0200	490.12	26.60
Xiaolongtan		0.6507	2.4000		3.86
	Fe ³⁺	0.3591	0.9700		6.67
	Fe ₃ O ₄	0.2918	-0.0200	495.55	42.59
		0.6328	0.0551	457.00	35.36
	α -Fe ₂ O ₃	0.4051	-0.1533	515.02	8.36
	γ -Fe ₂ O ₃	0.6281	0.8400		10.61
	Fe ³⁺ -silicate	0.3838	2.4000		2.83

^a δ = Isomer shift values relative to α -iron, Δ = quadrupole splitting, H = magnetic hyperfine field. ^b Values given are within ± 0.0001 of actual values.

ash originate from Fe²⁺ sulfates (szomolnokite, rozenite, and melanterite) in coal.³⁰ The occurrence of iron oxides in fly ash is due to the transformation of Fe sulfides and sulfates. Hematite content is dramatically raised in fly ash because of the oxidation of Fe sulfides, sulfates, carbonates, and magnetite, as well as some dehydroxylation of goethite and lepidocrocite.^{19,28} Spinel normally has a constant proportion in fly ash, and its high concentration in some samples is probably a result of secondary spinel formation at the expense of Mg, Al, and Fe oxides or recrystallization of clay and mica minerals.³⁸

The minerals and phases of ferrospheres extracted from the fly ashes of five power plants are examined using XRD and Mössbauer spectroscopy, which are given in Figures 7 and 8. The ferrosphere phase-mineral compositions commonly include Fe-rich aluminosilicate glass, magnetite, hematite, magnesioferrite, quartz, mullite, and ferrian spinel. Other accessory minerals containing Fe, Mg, and Ti also occur in the fractions. Magnetite, hematite, and magnesioferrite are the main iron-bearing minerals of ferrospheres; a clear spike of glass phase is also identified in ferrospheres.

Mössbauer spectroscopic investigation has been applied by various workers to study these iron-bearing minerals in complex samples because it has certain distinct advantages over many other techniques.¹⁰⁻¹⁹ Typical Mössbauer spectra of ferrospheres samples obtained from fly ashes in three power plants are shown in Figure 8. The spectra of all the as-received samples consist of several doubles, each characterized by the isomer shift (δ), the quadrupole splitting (Δ), the magnetic hyperfine field (H), and the relative area (%).

The Mössbauer parameters obtained for the iron speciation are shown in Table 3. It can be concluded that iron in ferrospheres is mainly present as Fe₃O₄, α -Fe₂O₃, γ -Fe₂O₃, and Fe³⁺-glass. From the areas of the doublets for various samples, it can be found that Fe₃O₄ has the maximum proportion in the samples, referred to as the relative area; for Jiaozuo, it is 84.31%; Yaomeng, 62.9%; and Xiaolongtan, 77.95%. γ -Fe₂O₃ is observed only in the samples from Xiaolongtan.

The concentrations of iron components vary from power plant to power plant. Different species of iron are formed in different boilers and combustion conditions, which are related to the combination of iron-bearing components and silicates in different temperatures and oxidizing or reducing conditions. The

Table 4. Chemical Compositions of Ferrospheres in Fly Ash (normalized to 100%)

ferrosphere type	Fe content (wt %)	Al + Si content (wt %)
ferrooxides	Fe \geq 75	Al + Si \leq 25
aluminosilicate-bearing ferrooxides	75 > Fe \geq 50	25 < Al + Si \leq 50
high-ferri-ferrous aluminosilicates	50 > Fe \geq 25	75 \geq Al + Si > 50
ferroaluminosilicates	Fe < 25	Al + Si > 75

species of iron in ashes reflects the thermodynamic behavior of the iron-bearing particle and the operation mode of the boiler.

Chemical Composition of Ferrospheres in Fly Ash. More than 60 ferrospheres with different structures are analyzed by EDX. The composition of each ferrosphere, normalized to three elements (Fe, Al, Si), is plotted in a ternary diagram (Figure 9). On the basis of the iron content, we can classify the ferrospheres in fly ash into four groups (Table 4): ferrooxides (Fe \geq 75%), aluminosilicate-bearing ferrooxides (75% > Fe \geq 50%), high-ferri-ferrous aluminosilicates (50% > Fe \geq 25%), and ferroaluminosilicates (Fe < 25%).

The type of ferrooxides with a high concentration of Fe (Fe \geq 75%) is present mainly as ferrooxide crystallized minerals. The XRD patterns have demonstrated that the ferrospheres are mainly composed of hematite, magnetite, and magnesioferrite (Figure 7). And the results of EDX show that there may be some Fe²⁺ included in oxides as amorphous phases. The transformations of iron-bearing minerals are related to the combustion conditions, and the valences of iron rely on the oxygen concentration and temperature of the system. Under reducing conditions with high temperature, iron mainly occurs as Fe²⁺. The study of McLennan shows that pyrite decomposes to pyrrhotite and then oxidizes from the surface inward to produce a molten FeO–FeS phase at 1353 K, which oxidizes to hematite and magnetite under oxidizing conditions but remains as FeO–FeS or FeO under reducing conditions.⁷⁷ The Fe²⁺ compounds become molten under low temperature and adhere to the heat-exchange surface easily, which is believed to have a significant impact on the formation of slags.

Along with rising temperature during coal combustion, iron-bearing minerals and clay minerals are melted and mixed to form aluminosilicate-bearing ferrooxides (75% > Fe \geq 50%). Most of the ferrospheres as shown in Figure 10e belong to this type and are derived from the fusion of inherent minerals of coal.

High-ferri-ferrous aluminosilicates (50% > Fe \geq 25%) are formed by the fusion of equal amounts of clay minerals and iron-bearing minerals. The XRD and FSEM-EDX studies show that iron in high-ferri-ferrous aluminosilicates mainly occurs as Fe-rich glass. The Fe²⁺-enriched compounds are the fusing agents of aluminosilicate particles; the fusion mixture, at a considerably lower temperature, and the fusant will condense and nucleate to form iron-rich initial layers and then deposit on the surface of the water wall tube.

The ferro-aluminosilicates (Fe < 25%) mostly originate from the fusion of clay minerals and a few iron-bearing minerals.

The content of Fe in deposits is very high;⁶¹ they may belong to the ferrooxide or aluminosilicate-bearing ferrooxide group. Mössbauer spectroscopy has demonstrated that much of the iron in the outer layers of the deposits is contained in aluminosilicate glass,⁷⁸ which may belong to the aluminosilicate-bearing fer-

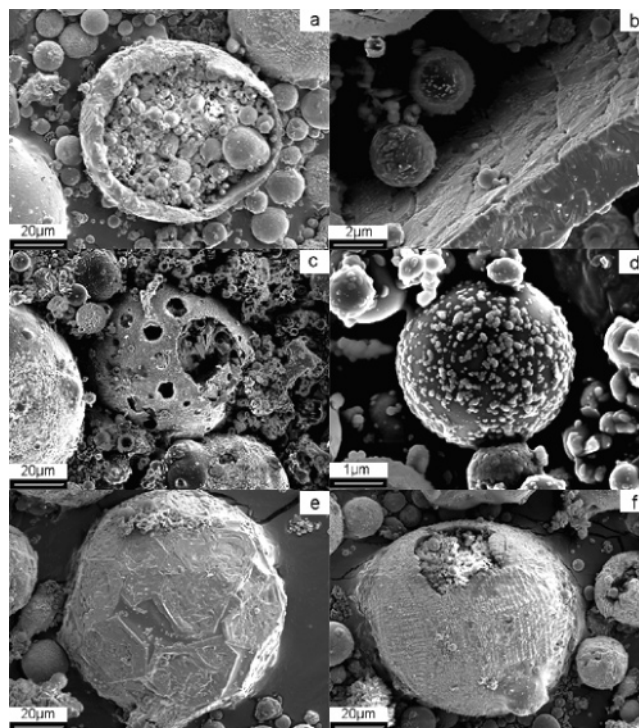


Figure 11. SEM images of ferrospheres (secondary electrons): (a) ferrospheres; (b) wall of ferrospheres; (c) porous ferrospheres; (d) molten drop ferrospheres; (e) ferrospheres with octahedral Fe oxide crystallization; and (f) dendritic ferrospheres.

rooxide group. Ferrooxides and aluminosilicate-bearing ferrooxides are important sources of the initial layer that occurs in deposits formed in coal combustion systems. Preferential deposition of liquid iron sulfides followed by in situ oxidation is believed to be the mechanism of deposit formation.⁷⁸ The deposition of molten pyrrhotite together with silicates results in an iron silicate deposit with a very low melting point, which accounts for the molten characteristics of the slag.

Microstructure of Ferrospheres in Fly Ash. The FSEM-EDX ferrospheres microstructures are shown in Figures 10 and 11. A general view of ferrospheres is shown in Figure 10a. Most of the ferrospheres have rough surfaces, and their shapes are close to that of an ideal sphere. There are often a large number of microspheres adhering to their surfaces. The morphology of the ferrospheres is varied. Some particles exhibit sheet crystalline morphology (Figure 10b) and some particles are smooth (Figure 10d), whereas others are not absolutely spherical but contain holes (Figure 11c), dendritic structures (Figure 10c, 11f), or granular structures (Figure 10e). According to the microstructure characteristics, the ferrospheres in fly ash can be divided into seven groups, namely sheet ferrospheres, dendritic ferrospheres, granular ferrospheres, smooth ferrospheres, ferrospheres, porous ferrospheres, and molten drop ferrospheres.

Among these ferrospheres, sheet ferrospheres are composed of a series of sheets (Figure 10b), and indications of layered morphology are visible. The results of EDX show that ferrooxide is the main component, which may be formed immediately by the oxidations of iron-bearing minerals.

The diameters of dendritic ferrospheres with a lot of ferri-spinel aggregates arrayed as branches on the surface vary from 10 to 80 μ m (Figures 10c and 11f). EDX analyses show that the narrow interspaces between skeleton branches are filled with aluminosilicate glass and that ferri-spinels are complex solid solutions based on FeFe₂O₄ with impurities of MgFe₂O₄.³⁸

(77) McLennan, A. R.; Bryant, G. W.; Stanmore, B. R.; Wall, T. F. *Energy Fuels* **2000**, *14*, 150–159.

(78) Huffman, G. P.; Huggins, F. E.; Shah, N.; Shah, A. *Prog. Energy Combust. Sci.* **1991**, *16*, 243–251.

Smooth ferrospheres are often less than 10 μm (Figure 10d). Little Fe is discovered in these ferrospheres, and they belong to the ferroaluminosilicate group.

For most cases, the external surface of the granular ferrospheres is rough, porous, and complicated by the additional presence of small granular crystals (Figure 10e,f). The diameters of small granular crystals with different structures vary from 0.5 to 2 μm (Figure 10f). The analyses of EDX show that the mineral phases are mainly ferrooxides as well as a few aluminosilicates. The granular crystals on the surface of the ferrospheres are predominantly a result of crystallization when the temperature decreases.

Hollow spheres packed with smaller spheres have been referred to as plerospheres. A 40 μm diameter ferroplerosphere observed in the samples is shown in Figure 11a and Figure 11b. The fine particles ($<5 \mu\text{m}$) packed inside have various sizes and shapes. The internal structure of the plerosphere is complex. From the analysis of EDX, it can be concluded that the Fe content of the fine particles is lower than that of the plerospheres and that they belong to the ferroaluminosilicate group. The thickness of the plerosphere wall varies from 1 to 5 μm , and the Fe content in the section of wall is higher than that on the surface. Further research is needed to understand the mechanism of plerosphere formation. Because plerospheres are packed with fine spheres, they are big enough to be captured by pollution control equipment easily.

Most porous ferrospheres belong to the fraction of microspheres of medium size ($d = 20\text{--}50 \mu\text{m}$; Figure 11c). The results of EDX show that the Fe content in the holes is higher than that in other areas of the surface; the Si–Al content is lower too. Porous ferrospheres are the complex eutectics of the iron-bearing minerals and clays.

The molten drop ferrospheres with a great deal of globlet particles on the surface are different from granular ferrospheres, and the globlet may be from the liquid melt of the inner particles (Figure 11d).

Moreover, some ferrospheres with octahedral ferrooxide have also been discovered (Figure 11e). The iron-bearing minerals and phases in fly ashes, which occur as ferro-ferrispheres, grains, crystals, aggregates, and agglomerates with sizes in the 1–100 μm range, have confirmed previous studies.^{38,43} The formation causes of these seven types of ferrospheres are considered to be different. Spherical particles are most often formed during high temperature. Crystalline grains on the surfaces of ferrospheres should come from the vaporization of inherent minerals. The aggregates and agglomerates maybe come from a combination of iron-bearing minerals and other minerals that undergo a complex transformation process in the boiler. The surface geometry of ferrospheres and the sizes of the crystallites depend

on the temperature and duration time of coal combustion, as well as the combination degree of iron-bearing minerals and other minerals or coal matrix. The major source responsible for the formation of ferrospheres is the minerals in raw coal, namely iron-bearing sulfides, sulfates, carbonates, and so on. The morphology and composition of ferrospheres (Figures 10 and 11) in fly ashes also strongly indicate that some of them are pseudomorphs after pyrite-marcasite crystals, aggregates, and framboids, and siderite concretions observed in coal.^{43,44}

Conclusions

There are more than 45 iron-bearing minerals in coal, as well as many other minerals containing Fe as impurities. More than 30 iron-bearing minerals were identified in fly ash, and the ferrospheres mainly include Fe_3O_4 , $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, MgFe_2O_4 , Fe^{3+} –glass, and ferrian spinel. Other accessory minerals containing Fe, Mg, and Ti also occur in these fractions.

Seven microstructures of ferrospheres are classified: (1) sheet ferrospheres, (2) dendritic ferrospheres, (3) granular ferrospheres, (4) smooth ferrospheres, (5) ferroplerospheres, (6) porous ferrospheres, and (7) molten drop ferrospheres. Most ferrospheres were spherical particles with microspheres found on their surfaces. Among them, sheet ferrospheres are formed by the oxidation of iron-bearing minerals; smooth ferrospheres, molten drop ferrospheres, ferroplerospheres, and porous ferrospheres are the complex eutectics of iron-bearing minerals and clays; and dendritic ferrospheres and granular ferrospheres are mainly formed by the conglutination after the oxidation of iron-bearing minerals.

On the basis of the iron content, we can classify the ferrospheres in fly ash into four groups: (1) ferrooxides, (2) aluminosilicate-bearing ferrooxides, (3) high-ferriferous aluminosilicates, and (4) ferroaluminosilicates. Ferrooxides are derived from the oxidation of iron-bearing minerals that are not mixed with aluminosilicates; aluminosilicate-bearing ferrooxides, high-ferriferous aluminosilicates, and ferroaluminosilicates are formed by the fusion of different proportions of inherent iron-bearing minerals and clay minerals. Ferrooxides and aluminosilicate-bearing iron oxides are important sources of the initial layer that occurs in deposits of coal-burning boilers.

Acknowledgment. This research was supported by the National Basic Research Program of China (2002CB211602, 2006CB200304) and the National Natural Science Foundation of China (NSFC) (90410017). The authors acknowledge Dr. Chen-lin Chou for his comments. Also, they thank Prof. Colin R. Ward and Dr. Stanislav V. Vassilev for providing many useful references.

EF060008F