



Characteristics of ferrospheres in fly ashes derived from Bokaro and Jharia (Jharkhand, India) coals

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ABSTRACT

Coal burning power plants in the state of Jharkhand, India, are facing the problem of fly ash landfilling and their economic and environmental impact. However, fly ash may be used in civil engineering constructions, including as geoliners for municipal wastes landfilling, however in this case the groundwater contamination should be taken in consideration.

In this work a combination of analytical techniques is used to study the nature, composition and potential environmental impact of Fe-bearing morphotypes (ferrospheres) in fly ash from thermal power plants fed with coals from Bokaro and Jharia coalfields (Jharkhand, India).

The results show that the feed coals are sulfur-poor and ash-rich, dominated by quartz, clays and minor portions of Fe-bearing carbonates, such as siderite. Pyrite was not identified. Although iron is present in the fly ashes in significant proportions (from 2.7 wt.% to 4.5 wt.%), equivalent to an Fe₂O₃ content ranging from 3.5 wt.% to 5.8 wt.%, mineral phases such as magnetite and hematite are only present in minor proportions, or below detection limits of the XRD analyses. Iron in the ferrospheres occurs as massive or dendritic crystals, or as finely dispersed crystals trapped inside a glassy aluminosilicate matrix resulting from the release of iron oxide plumes into the aluminosilicate melt. In addition to these phases, iron also occurs as a component of the glass that makes up most of the fly ash materials. Finally, the contaminant potential of groundwater by the fly ash iron is negligible.

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1. Introduction

Iron is a common element in coal and one of the main inorganic constituents of fly ash phases. It is generally associated with pyrite and/or siderite in the mineral matter of coal, and its evolution during heating in coal power plants is well understood, especially with respect to pyritic iron evolution (Raask, 1985).

In low-rank coals, i.e. lignites and sub-bituminous coals, some of the iron may be present in the form of organometallic complexes (Francis, 1961; Li et al., 2007, 2010; Raask, 1985). However, iron occurs mainly in the mineral-fraction of bituminous coals as sulfides, clays, carbonates, sulfates, and oxides and hydrated oxides (Raask, 1985):

- Iron disulfide (pyrite) is the most important of the iron bearing minerals in coal. However, other iron sulfides such as marcasite (FeS₂), chalcopyrite (CuFeS), melnikovite (FeS₂ + (As,Fes,H₂O)), mispickel (FeS₂·FeAs₂), and pyrrhotite (Fe_(1-x)S) may also occur in coals

(Raask, 1985; Ward, 2002). Minerals as ferroselite (FeSe₂), and eskebornite (CuFeSe₂) may also occur in coal but were inferred from scanning electron microscopy with X-ray microanalysis (SEM/EDS), and not detected by X-ray diffraction (XRD) (Dai et al., 2015). The occurrence of such phases is mainly influenced by the relative abundance of sulfur and the fixation of sulfur by anaerobic bacteria. The sulfur may have an organic origin or be brought in by marine waters in the form of sulfates. Silicates weathering typically provides the iron for the formation of syngenetic pyrite (Neavel, 1966; Chou, 2012, and references therein);

- Iron-bearing sulfates include a number of hydrated ferrous and ferric sulfates occurring in weathered coals, such as coquimbite (Fe₂(SO₄)₃·9H₂O), jarosite (K₂SO₄·xFe₂(SO₄)₃), natrojarosite (NaFe₃(SO₄)₂(OH)₆), melanterite (FeSO₄·7H₂O), rozenite (FeSO₄·4H₂O), szomolnokite (FeSO₄·H₂O), roemerite [FeSO₄·Fe₂(SO₄)₃·14H₂O], and halotrichite [FeAl₂(SO₄)₄·22H₂O] (Kossenber and Cook, 1961; Ehlers and Stiles, 1965; Gluskoter and Simon, 1968; Gruner and Hood, 1971; Rao and Gluskoter, 1973; Gluskoter, 1977; Ward, 2002; Chou, 2012);

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- Clay minerals, such as illite ($(K_{1.5}Al_4(Si_{6.5}Al_{1.5})O_{20}(OH)_4$ with Fe) and chlorite ($(MgFeAl)_6(AlSi)_4O_{10}(OH)_8$), namely chamosite and clinocllore (Dai and Chou, 2007), are the most common iron-bearing silicates in coals. Where present, illite is commonly a clastic mineral brought in by water to the peat swamp (Dixon et al., 1970; O'Gorman and Walker, 1972; Raask, 1985; Rao and Gluskoter, 1973); however, illite and chlorite may also be formed by diagenetic processes in some coal seams (e.g. Permana et al., 2013);
- Carbonates such as siderite ($FeCO_3$) and ankerite ($CaCO_3 \cdot FeCO_3$) are the most common iron-bearing carbonates. Siderite is chiefly a syngenetic carbonate while ankerite is mostly epigenetic, i.e. a product formed of later-stage mineralization process (Stach et al., 1982; Permana et al., 2013);
- Iron oxides and hydrated Fe-oxides in coals may include magnetite (Fe_3O_4), hematite (Fe_2O_3) and limonite ($Fe_2O_3 \cdot H_2O$) (Raask, 1985).

During the burning of coal these iron-bearing phases may undergo transformations, forming crystalline phases such as magnetite and hematite (Anshits et al., 1998, 2000, 2001; Raask, 1985; Vassilev and Vassileva, 1996a, 1996b) or interacting with other components such as clay mineral residues to form an amorphous, iron-bearing aluminosilicate glass (Matjie et al., 2011; Sokol et al., 2000, 2002; Ward and French, 2006).

Ferrospheres (also known as magnetic microspheres or magnetite globules), as initially proposed by Lauf (1982) and Lauf et al. (1982), are highly reflective spherical particles seen in cross sections under reflected white light microscopy, which are characterized by their iron content, density and magnetic properties as being composed of magnetite and hematite (Bibby, 1977; Hansen et al., 1981). Magnetite is a spinel (nominally Fe_3O_4) derived from glass particles containing fine magnetite (Fe_3O_4) precipitates (Lauf et al., 1982), which originated after crystallization from melts derived from illite and pyrite (Raask, 1985), or just pyrite, corresponding to the eutectic ($T = 1070^\circ C$) of wüstite–fayalite ($FeO-Fe_2SiO_4$), with a total content of up to 80 wt.% FeO (Anshits, 1998, 2000, 2001; Sokol et al., 2000, 2002).

Ferrospheres have been classified on the basis of the iron oxidation state, iron content and morphology based on their three dimensional surface topography seen under secondary electron detection mode on scanning electron microscopy (SEM):

- According to the type of iron (Fe^{2+} or Fe^{3+}) ferrospheres may be divided into:
 - (i) *Ferrospheres*, essentially composed of magnetite (ferrous–ferric oxide);
 - (ii) *Ferrispheres*, essentially composed of hematite and limonite (Vassilev and Vassileva, 1996b);

On the basis of the iron content Zhao et al. (2006) divided the ferrospheres into ferrooxides ($Fe \geq 75\%$), aluminosilicate-bearing ferrooxides ($75\% > Fe \geq 50\%$), high-ferriferous aluminosilicates ($50\% > Fe \geq 25\%$), and ferroaluminosilicates ($Fe < 25\%$).

- Based on their appearance under the SEM, Anshits et al. (2011) divided the ferrospheres into five main morphologic types: porous (foam-like); glass-like; dendritic; skeleton-dendritic; and block-like. Apart from the size and form of the Fe-crystals this classification also reflects the changes in the aluminosilicate matrix from the foam-like to the block-like morphology.
- Also based on SEM studies, Zhao et al. (2006) classified the ferrospheres into seven groups according to their microstructure: sheet ferrospheres, dendritic ferrospheres, granular ferrospheres, smooth ferrospheres, ferroplerospheres, porous ferrospheres, and molten drop ferrospheres.
- Among the most common carbonate minerals occurring in coal (siderite, ankerite, dolomite and calcite), siderite is the first to

dissociate during combustion, forming wüstite ($FeCO_3 \rightarrow FeO$ (wüstite) + CO_2) (Raask, 1985) under reducing conditions, which then oxidizes to magnetite (Fe_3O_4) or hematite (Fe_2O_3) (Powell, 1965; McLennan et al., 2000). However, as a result of the rapid CO evolution, siderite particles in contact with aluminosilicates may disintegrate into 0.1 μm to 1.0 μm fragments; the resulting iron oxide is highly reactive and readily combine with the aluminosilicate melt forming Fe spinels or enriching the aluminosilicate glass with Fe (Raask, 1985; McLennan et al., 2000; Creelman et al., 2013).

Ferrospheres and other Fe-bearing morphotypes may also occur in fly ash from pyrite-poor coals. However, they are mostly ignored in such cases, probably because of their low-proportions, and the consequent lack of relevance for technological applications and hence their low economic value, which tend to discourage more detailed study. However, the Indian fly ashes covered by this work are being studied for use as a geoliner material (Shreya and Paul, 2015; Shreya et al., 2014, 2015), and such newly formed Fe-bearing minerals may contribute to the environmental impact of ash use. Therefore, the genesis and characteristics of the ferrospheres may have some relevance to the use of the ashes in this way.

The properties of coal fly ash are a function of several variables such as the coal source, the degree of coal pulverization, the design of the boiler unit, the loading and firing conditions, and the handling and storage methods (Mandal and Sengupta, 2002; Baba, 2003; Department of Forests et al., 2007; Valentim and Hower, 2010). An overall understanding of fly ash mineralogy, geochemistry and leaching behavior should be obtained to complement the understanding about ferrosphere genesis, and their potential impact, for example in geotechnical applications. For that purpose a set of techniques are commonly used to study the fly ash as a whole or its components:

- The nature and proportion of both the crystalline (mineral) and non-crystalline or amorphous (glass) components can be obtained by X-ray diffraction (XRD) analysis (Ward and French, 2006). This technique is particularly useful to detect minor crystalline phases such as magnetite and hematite (Vassilev and Vassileva, 2005);
- Identification and characterization of the different phases in fly ash and their mode of occurrence at a particle-by-particle scale may be accomplished using scanning electron microscopy in conjunction with X-ray microanalysis (SEM/EDS) (Vassilev and Vassileva, 2005). The combination of SEM/EDS with petrographic techniques (polished blocks and observed under reflected white light microscopy) is a powerful method to obtain information on the individual components of the fly ash (Hower and Mastalerz, 2001; Hower et al., 2005; Suárez-Ruiz and Valentim, 2007; Suárez-Ruiz and Ward, 2008; Suárez-Ruiz et al., 2008a, 2008b, 2015; Lester et al., 2010; Hower, 2012);
- The major element concentrations can be determined by X-ray fluorescence (XRF), and the combination with XRD results allows to infer the glass composition (Ward and French, 2006).
- Leaching and pH studies are important in predicting the environmental impacts associated with ash disposal (Liu et al., 2009; Praharaj et al., 2002; Ward et al., 2009), especially the impact on water quality (EPA, 2000), and to follow the leaching behavior of a particular element in the fly ash over time using techniques such as XRF and inductively-coupled plasma mass spectrometry (ICP-MS) (Izquierdo and Querol, 2012; Kim and Hesbach, 2009; Liu et al., 2009; Ward et al., 2009; Xie et al., 2007). In the case of the Fe content, these studies may determine the removal, or not, of the iron-morphotypes, e.g. by magnetic methods.

In addition to these techniques Raman microspectroscopy (MRS), magnetic susceptibility (χ), isothermal remanent magnetization (IRM), and Mössbauer spectroscopy (MS) are very useful for the ferrospheres in fly ashes studies. MRS offers the possibility of performing 1 μm^2 analysis areas of the fly ash morphotypes to obtain information concerning the mineral phase present, and may be used to

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