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Physical–chemical characteristics and elements enrichment of magnetospheres from coal fly ashes

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HIGHLIGHTS

- The detailed mineralogy components of magnetospheres were investigated using Mössbauer spectrometer.
- The saturation magnetization of magnetospheres is proportion to their Fe_3O_4 content.
- The possible existence forms of trace elements enriched in magnetospheres were proposed.

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ABSTRACT

Nine magnetospheres samples were recovered by magnetic separation from fly ashes of typical coal-fired power plants in China and Russia, respectively. The physical–chemical characteristics of magnetospheres were investigated using particle size distribution instrument, BET surface area analyzer, physical property measurement system with vibrating sample magnetometer (PPMS-VSM), field emission scanning electron microscopy with energy-dispersive X-ray spectroscopy (FE-SEM-EDX), X-ray fluorescence (XRF), inductively coupled plasma mass spectrometry (ICP-MS), X-ray diffraction (XRD), and Mössbauer spectroscopy. The potential application and possible environmental concern of magnetospheres was also discussed. The results suggest that magnetospheres are superparamagnetism with a minimized coercivity and a negligible magnetization hysteresis. The iron species in magnetospheres mainly include Fe_3O_4, α-Fe_2O_3, γ-Fe_2O_3, Fe^{2+}-silicate, Fe^{3+}-silicate, and FeSi, while the content of each iron species are varied from different power plants. Magnetite (Fe_3O_4) is the dominant iron-bearing mineral, which governs the magnetic property of magnetospheres. The saturation magnetization of magnetospheres are proportion to their Fe_3O_4 content, and it can be described by the linear regression equations of $[M_s] = -21.4 + 0.71\ [Fe_3O_4]$ ($R = 0.89$). The magnetism of magnetospheres are also determined by the quantity of elements substituted for Fe and their respective magnetic moments in the spinel structure. The siderophile elements (Cr, V, Co, Ni), chalcophile elements (Cu, Zn) and lithophile elements (In, U) are obviously enriched in magnetospheres.

1. Introduction

Magnetospheres (magnetic fractions in fly ashes), as an enormous valuable resource in coal combustion products, could be easily recovered from fly ashes using both dry and wet magnetic separation [1,2]. Fly ash is produced about 750 million tons every year in the world [3]. The amount of magnetospheres in fly ashes ranges from 0.5% to 18% [4]. Thus even calculated the magnetospheres yields by 1%, the potential annual production of magnetospheres would exceed 7.5 million tons. Though the physical–chemical characteristics of magnetospheres have not been still adequately studied, some applications in metallurgy, catalysis, advanced functional materials, and other fields have been widely proposed [4–11]. For instance, because of the combination of magnetism and high temperature resistant together with stable chemical properties, magnetospheres are capable to be used as the substitutions of some advanced functional magnetic materials [4,7,11]. Due to the spinel structure, the promising application of magnetosphere was suggested as catalyst [5,6,9,12], whilst the enrichment of some transition metals (Ni, Cr, V, Co, Mn, Cu) also significantly affect its catalytic performance. Further, if the magnetospheres are not competent to the refining utilization presented above, the direct application may be successful in the substitution for high Fe ore in

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metallurgy, in the production of dense concrete, and in the production of ferrosilicon or the substitution for commercial magnetite [4,10].

Magnetospheres are mainly derived from the decomposition and oxidation of Fe-bearing minerals, such as pyrite, siderite, ankerite, and other Fe-bearing minerals, during coal combustion process [13–17]. Pyrite will be firstly decomposed to $Fe_{1-x}S$ under lower temperature [18], and the intermediate iron species will ultimately convert into α-Fe_2O_3 with the increase of combustion temperature under the following transformation sequence: pyrite → intermediate ferrous species → intermediate ferric species → α-Fe_2O_3 [13]. Intermediate iron species Fe_3O_4 is firstly oxidized to intermediate ferric species γ-Fe_2O_3 or the solid solution containing γ-Fe_2O_3 and Fe_3O_4, and then those iron species in transition state will ultimately convert into α-Fe_2O_3 [19]. However, Fe_2O_3 will be transformed into Fe_3O_4 again when the temperature reaches 1400 °C [19]. At high temperature together with reducing atmosphere, the iron species dominantly present as Fe^{2+}-bearing minerals; in contrast, at low temperature together with oxidizing atmosphere, the iron species are mainly present as Fe^{3+}-bearing minerals, including γ-Fe_2O_3, α-Fe_2O_3, Fe^{3+}-silicate, and so on [15].

Because of the complex formation process of magnetospheres, a lot of iron species including hematite, magnetite, maghemite, Fe^{2+}-silicate, Fe^{3+}-silicate, Ca and Ca–Mg ferrite spinel, and some accessory iron-bearing minerals, such as martite, mushketovite, wustite, ilmenite, chromite, native Fe, Mn ferrite, ferrosilicon, Fe hydroxides, $FeWO_4$, FeAsS, and F_3C, have been identified in magnetospheres [4,13,20–31]. The content of iron-bearing minerals in magnetospheres is varied from different fly ashes collected from different power plants, which strongly depends on the feed coals and combustion conditions. Magiera et al. [27] have observed that magnetite, magnesioferrite, and maghemite are the dominant ferrimagnetic minerals in most fly ashes of hard coal, while a considerably greater quantity of hematite and/or maghemite were/was observed in the fly ashes of lignite. Magnetospheres are also divided into two types: ferrospheres and ferrispheres, which are amorphous, crystalline and mixed Fe-enriched aluminosilicate spheres concentrated, respectively, in Fe^{2+} or Fe^{3+} in glass and minerals [32,33]. However, the quantitative amount of various iron species present in magnetospheres has not been still understood systematically.

The microstructure and chemical composition of magnetospheres also have been conducted using different techniques [4,5,21,22,34]. It is very important to understand the microstructure of magnetospheres since it not only gives an idea about the shape of magnetospheres but also gives some valuable clues about the mineralogical phases present in magnetospheres [2,4,8,16,21,23,35–43]. By analyzing the composition of magnetospheres, different morphologic types of magnetospheres were identified including massive globules (CaO + MgO)-rich magnetospheres and porous globules (SiO_2 + Al_2O_3)-rich magnetospheres [36]. Massive magnetospheres are generally occurred as coarse crystalline spinel structure, while fine crystalline dendrite spinel formations are more common in porous globules [36]. Based on the microstructure, the magnetospheres have been classified into seven typical groups: sheet magnetospheres, dendritic magnetospheres, granular magnetospheres, smooth magnetospheres, ferro-plerospheres, porous magnetospheres, and molten drop magnetospheres [44]. The factors that affect the formation of these magnetospheres with different microstructures are varied. The types of boilers and combustion condition have an important effect on their microstructures [8,23,43,44]. In particularly, the mineral components in feed coals will determine the size of magnetospheres, the thickness, porosity of their shells as well as the composition and morphology of the globules, and further to play a leading role in the viscosity of the melt and the surface tension change [41].

The transformation process of iron-bearing minerals in feed coals has been focused in many studies. However, there was still a lack of systematic interpretation of physical–chemical characteristics of magnetospheres for the refining utilization, especially for those magnetospheres from coal-fired power plant fly ashes in China. Therefore, in this work, the physical–chemical characteristics of magnetospheres, such as the particle size distribution, the BET surface area, the magnetism, the microstructure, the chemical composition, the enrichment of trace elements, and the mineralogy were detailed studied. The distribution of 44 trace elements (Li, Be, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Nb, Mo, Cd, In, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ta, W, Re, Tl, Pb, Bi, Th, U, Zr, Hf) in various fractions of fly ashes (magnetospheres, non-magnetic fractions and raw fly ashes) was investigated in details. Special attention was paid to the relationship between magnetism and iron-bearing minerals so as to identify the general regularities and individual features governing the magnetic properties of the magnetospheres. The potential applications and possible environmental concerns of magnetospheres were also discussed.

2. Experimental section

2.1. Samples collection and magnetic separation

Eight fly ash samples were collected from the hoppers of electrostatic precipitators of typical pulverized coal-fired power plants (Huangshi, Zhujiang, Ezhou, Shiheng, Luohe, Shajiao C, and Beijing) in China and Russia (Primorskay'a power plant), as shown in Fig. 1. The magnetospheres were separated from fly ashes using wet magnetic separation. In this work, different amount of magnetospheres in fly ashes were separated varying in the range from 1.5% to 11.5% (presented in Table 1). The refined magnetospheres sample separated from Huangshi magnetospheres was also investigated, which were isolated using a three-step separation process [8]. General information about the power plants for investigation was presented in Table 1.

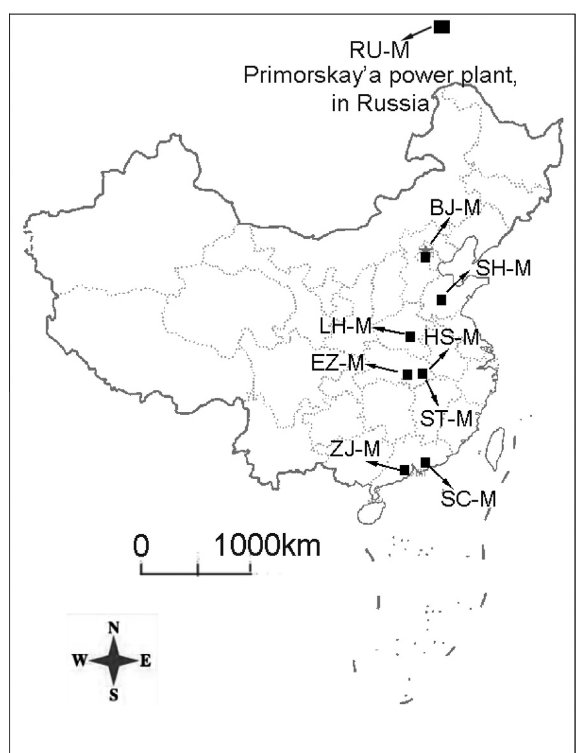

Fig. 1. Location of coal-fired power plants for fly ashes collected.