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IRON OXIDES PARTICLES IN THE AIR AND FLY ASH, AND THEIR INFLUENCE ON THE ENVIRONMENT (PRELIMINARY STUDIES)

Mariola JABŁOŃSKA[1], Danuta SMOŁKA-DANIELOWSKA[1]

Abstract. The paper presents preliminary data concerning sizes, distribution and composition of the most popular particles, which are formed during coal combustion, i.e. iron oxide particles. It is written only about particles of iron oxides, not describing different phases which contain iron (such as sulphides, carbonates or native iron). Particles of PM10 (Particule Matter 10) and the fallen dust were collected in several towns of the Upper Silesia. Fly ash samples from the coal combustion were separated in electrofilters. All samples were gathered during the last years. Samples were analysed by X-ray diffraction on Philips PW 3710 instrument (with CoKα radiation) and Philips XL30 TMP scanning electron microscope equipped with EDAX system and EDS type Sapphire.

In fly ashes, similar iron oxide particles were found. However, differences in concentration of accessory components were observed. The magnesioferrite, hercynite and chromite occurred in the fly ashes.

Differences were also observed in grain size of the dominating particles. About 50–60 wt. % of iron oxides particles present in the atmospheric dust have diameters less then 10 mm, while about 10 wt. % of them show particles less then 2.5 mm (respirable particles). The fly ashes from the electrofilters contained a lot of iron oxide particles with the diameter range 30–80 mm (average about 70 wt. % of all iron oxides particles).

Most of larger iron oxide particles originating from the coal combustion are separated in the electrofilters, but the smallest fractions (less then 10 mm) are emitted to the atmosphere. Since a lot of iron oxides particles, which diameters is less than 10 mm are observed in the air it may be assumed that these diameters are transported to long distances. Moreover, iron oxide particles which diameters are less then 2.5 mm can show a potential hazard to human health. There are preliminary studies of iron oxides, which will be continued.

Key words: iron oxides, atmospheric dust, fly ash, pollution, Upper Silesia.

Abstrakt. Niniejszy artykuł przedstawia wstępne wyniki badań dotyczące rozmiarów, rozmieszczenia i składu najczęściej występujących cząsteczek o składzie tlenków żelaza, które powstały podczas procesów spalania węgla kamiennego. Opis dotyczy tylko wyżej wymienionych cząstek natomiast pominięto inne fazy zawierające żelazo (takie jak siarczany, węglany czy też żelazo metaliczne). Cząsteczki PM 10 (pył zawieszony) oraz pył opadowy pobrane były w kilku wybranych miastach Górnego Śląska. Próbki popiołu pobrano z elektrofiltrów zakładów spalających węgiel kamienny. Wszystkie próbki zebrano w ciągu kilku ostatnich lat. Materiał badawczy poddano analizie rentgenowskiej metodą proszkową, wykorzystując dyfraktometr Philips PW 3710, używając lampy kobaltowej CoK_{α} oraz badaniom w skaningowej mikroskopii elektronowej przy użyciu środowiskowego mikroskopu Philips XL30 TMP wyposażonego w EDS typu Sapphire.

Dominujące cząsteczki tlenków żelaza (magnetyt, hematyt, wustyt) obserwowano w pyłach atmosferycznych i popiołach z elektrofiltrów. Różnice obserwowano w ilości i składzie cząstek akcesorycznych. W popiołach częściej występowały: magnezioferryt, harcynit i chromit.

Różnice obserwowano też w rozmiarach dominujących cząstek. Tlenki żelaza w pyłach atmosferycznych o średnicach poniżej 10 mm stanowiły ok. 50–60% obj., podczas gdy cząstki o średnicach respirabilnych (poniżej 2,5 mm) to ok. 10% obj. Popioły z elektrofiltrów zawierają cząstki tlenków żelaza o średnicach rzędu 30–80 mm (co stanowi ok. 70% obj. wszystkich cząstek o składzie tlenków żelaza). Większość dużych cząstek tlenków żelaza powstających w procesach spalania węgla kamiennego osadza się na elektrofiltrach, jednak najmniejsze frakcje (poniżej 10 mm) są emitowane z gazami spalinowymi do atmosfery. Stąd w powietrzu odnotowuje się znaczne ilości tlenków żelaza o średnicach mniejszych niż 10 mm co powoduje,

[1] Faculty of Earth Sciences, University of Silesia, Będzińska 60, 41-200 Sosnowiec, Poland; e-mails: mjablons@us.edu.pl, dsmolka@wnoz.us.edu.pl

iż rozmiary tych cząstek sprzyjają dalekiemu transportowi od źródła ich powstawania. Natomiast cząstki zawierające tlenki żelaza o średnicach respirabilnych mogą niekorzystnie działać na zdrowie. Badania te powinny być kontynuowane celem szczegółowego określenia wpływu tlenków żelaza na środowisko i organizmy żywe.

S³owa kluczowe: tlenki żelaza, pył atmosferyczny, popiół lotny, zanieczyszczenie, Górny Śląsk.

INTRODUCTION

A fly ash and a slag are solid products of coal burning, a mineral composition of which depends, to a large degree, on physical and chemical properties of coal, its petrographic composition and the mineral contamination (Misz, 2002). It is estimated that the fly ash represents 75–85% of the total mass of wastes produced in heat and in heat and power stations in the process of coal burning (Laudyn *et al*., 1997). Estimated data indicate that 300–400 kilograms of wastes from heat and power stations are produced out of one tonne of the combusted coal, whereas in case of the burning of coal of poor quality coal combustion, the amount of the ash may reach up to 50% (Bojakowska, 1994).

In 2000 the total dust emission in the Upper Silesia amounted to 24% of the total dust emission in Poland (Szymańska-Kubicka *et al*., 2001). The concentrations of respirable particles in the Upper Silesia were relatively high in comparison with industrial areas in Western Europe and the United States (Pastuszka, 2001).

Pollution emitted to the atmosphere by the heat and power stations causes a number of negative effects in the environment. The process of hard coal burning releases huge amounts of dusts. Due to their fine-dispersion nature (50–80% the particles with of < 10mm diameter in size), they may be transported at long distances and deposited in areas not necessarily in the immediate neighbourhood of the emitters (Nowak, Kwapuliński,1991; Żelechower *et al*., 1998).

Spherical forms of dusts, characteristic of the professional power engineering, are seen on the surface of both buildings and rocks in areas with a relatively low level of atmospheric pollution (Wilczyńska-Michalik, Michalik, 1996).

Morphology and chemical composition of fine-dispersion pollution released in the process of hard coal burning is of great importance with respect to the environmental protection. The particles of the atmospheric dust, which contained iron oxides and have diameters less then 2.5 mm can be potentially hazardous to human health.

METHODS

Particles of PM10 and fallen dust were collected in several towns of the Upper Silesia. Particulates of deposited dust were allowed to accumulate in glass jars with a volume of 1×10^3 cm^3 for one month at 2.5 m above a ground level. The samples of airborne dust were collected at a height of 2.5 m on borosilicate glass covered by Teflon filters using an automatic TEOM 1400 sampling device.

The material under investigation is the fly ash produced in the process of coal burning and collected by electrofilters (effectiveness of waste gas collection 95–98%) in selected heat and power stations located in the Upper Silesia.

The fly ash was produced as a result of coal burning in steam and water boilers. The temperature in the combustion chamber was between 950 and 1200°C.

All grain sizes of the suspended particles and settled dust were measured in two dimensions using calibrated scanning electron microscopy (with a relative error of 10%). A size of particulates is determined as a root-mean-square size, $r.m.s. = \left\{a^2 + b^2\right\}^{\frac{1}{2}}$, where *a* and *b* are two orthogonal dimensions across the grain (Rietmeijer, Janeczek, 1997).

The samples were examined by X-ray powder diffraction in Geigerflex Rigaku-Denki and Philips PW 3710 diffractometers in aim to determine the abundance of the most common crystalline components of the atmospheric dust and fly ash.

All samples were also examined by scanning electron microscopy Philips XL30 TMP operated in the environmental mode at 15 kV accelerating voltage and equipped with EDAX EDS system, type Sapphire. Samples of fly ashes were analysed by the optical reflected light microscope.

RESULTS AND DISCUSSION

The composition of the atmospheric dust and fly ashes and the grain size specified physical properties, which are of fundamental significance when defining an impact of a disposal site on the environment (pollution of the air and groundwaters). It also determines filtration and dusting properties. Many finer particles of the fly ash are emitted to the natural environment.

In the present research trials were done to trace the influence of iron oxide particles on the environment. A grain size of those particulates was analysed first.

Table 1

Grain size distribution of iron oxides (haematite, magnetite, wüstite) in fly ash

Range of diameters in microns		< 20	20–80	> 80
Iron oxides	% of total	21.75	23.75	44.50
	mean	2.10	8.50	16.50
	std.dev.	1.70	2.20	4.50

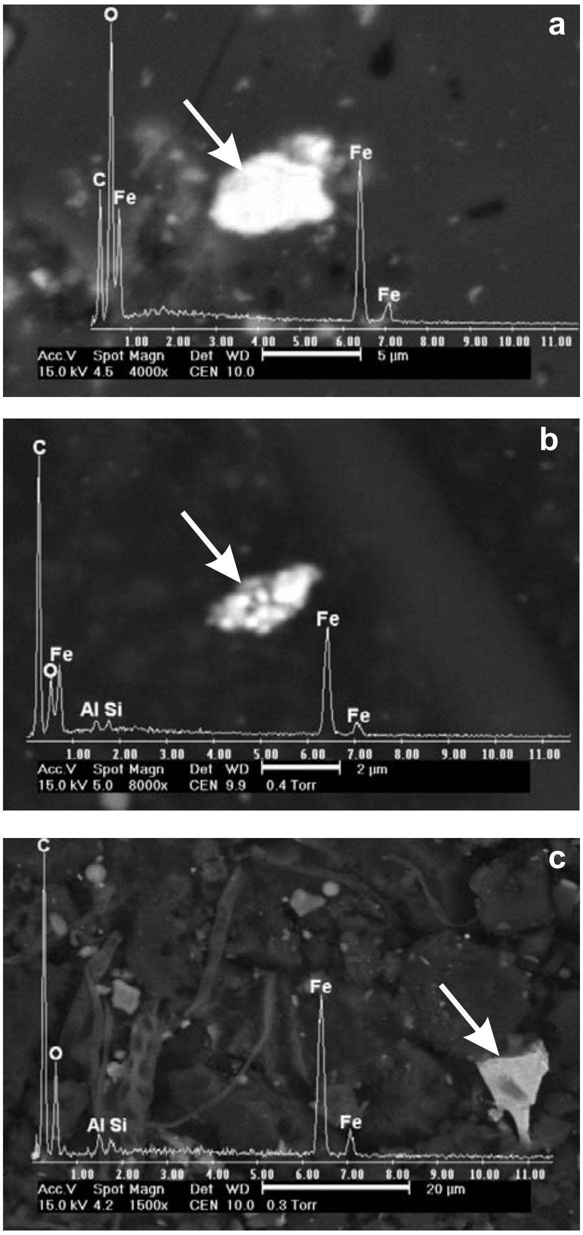

Fig. 1. Atmospheric particles of iron oxides from Chorzów (a), Katowice (b) and Sosnowiec (c)

BSE image; EDS spectrum

Table 2

Grain size distribution of iron oxides (haematite, magnetite, wüstite) as a function of season in settled dust from Upper Silesia (a summary for all locations)

Range of diameters in microns			<5	5–10	>10
Iron oxides:	summer season	% of total	61.5	21.5	17.0
		mean	2.25	7.38	15.96
		std. dev.	1.22	1.65	3.62
Haematite					
Magnetite	heating season	% of total	64.5	22.6	12.9
Wüstite		mean	2.56	7.15	17.40
		std. dev.	1.21	1.49	6.27

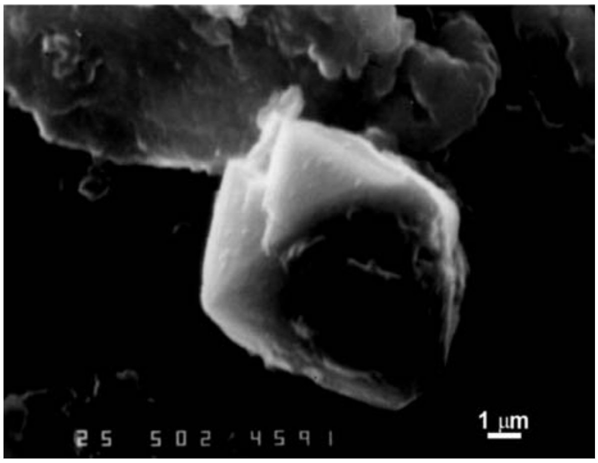

Fig. 2. Atmospheric particle of magnetite from Siemianowice Œl skie, BSE image

Many bigger fly ash particles (with a above 20 µm) are collected on electrostatic precipitators (Table 1), while the smaller particles penetrated into the air, as it results from one-year-observations (Table 2). Because the particles collected in the atmospheric dust have diameters approximately 10 µm (Fig. 1a, b, c), especially in the winter season, it may be suggested that the iron oxide particulates can be transported for a long distance from their sources. The particles of the atmospheric dust mostly have diameters below 5 µm and can be hazardous to a human health.

Particles which are composed of iron oxides (magnetite (Fig. 2), haematite and wüstite) are observed both in the atmospheric dust and the fly ash. Their chemical composition frequently differs from their natural analogue, being probably dependent on parameters of the coal combustion process and feed coal properties. The rest of the iron oxide particles, which are observed in the atmospheric dust pollutants have been similar to goethite and various spinels such as chromite, magnesioferrite, hercynite, franklinite, jacobsite.

The particles of magnetite and haematite, which were analysed in the atmospheric dust and in the fly ash, occur as spherical and oval forms (Fig. 3a, b, c), in most cases porous, with numerous hollows and ducts. They are characterised by a skeleton structure (Fig. 4) seen in the dendrite, fan- and rounded-shaped

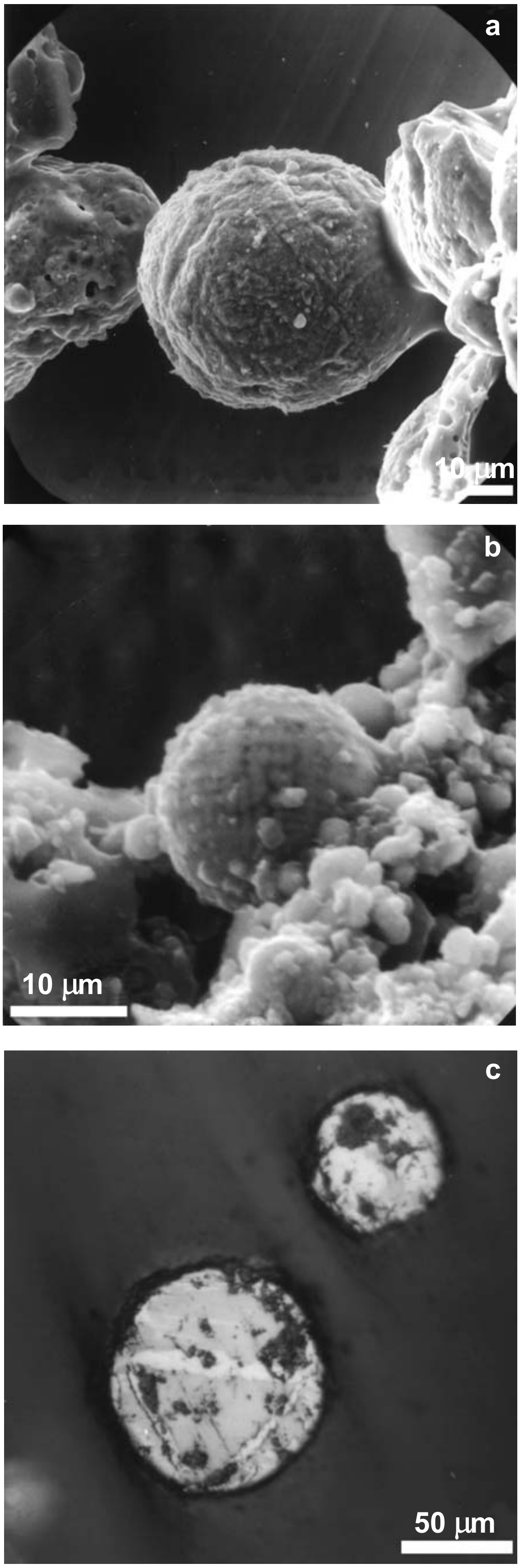

Fig. 3a, b — examples of iron oxides in the analysed fly ash in the heat and power stations in Upper Silesia (Poland) equipped with electrofilters; c — fan-shaped inclusions of magnetite and haematite in the aluminosilicate matter (reflected light); fly ash from the burning of bituminous coal in Upper Silesia (Poland)

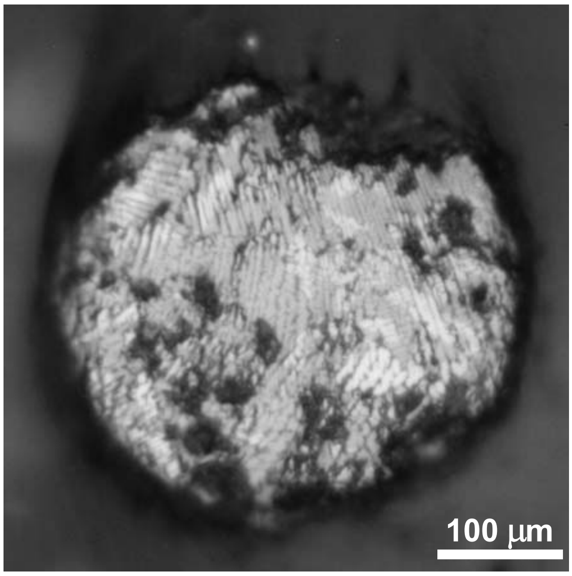

Fig. 4. Skeleton structure of magnetite and haematite particle (reflected light) from the fly ash from the heat and power stations in Upper Silesia (Poland)

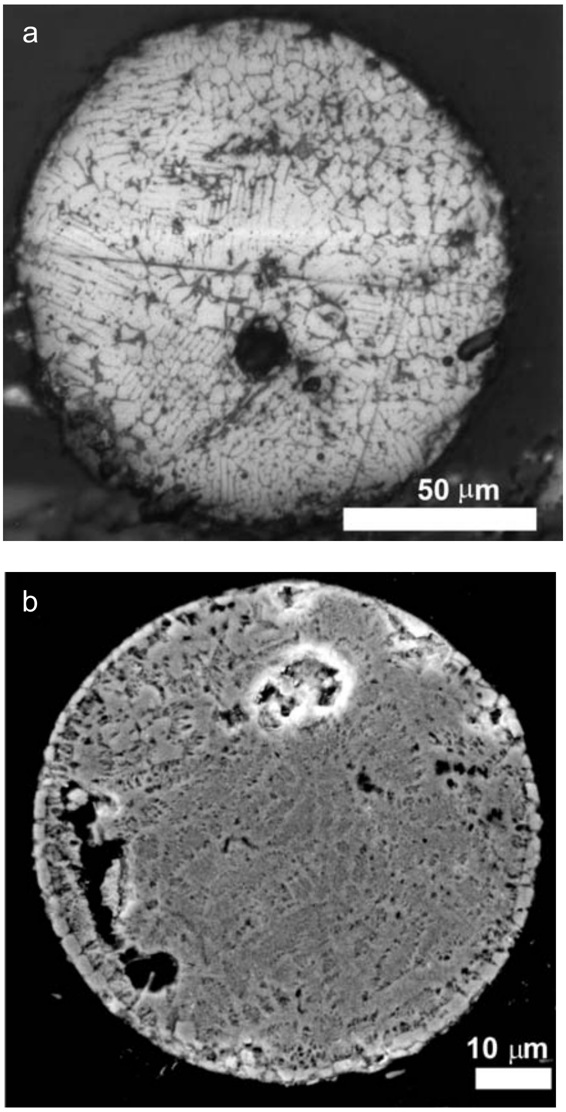

Fig. 5. Dendrite structure of fly ash particle (a) and atmospheric dust particulate (b)

forms (Fig. 5a, b). Some particles are empty inside but they are spherical. That type of particles formed in smaller amounts.

The iron oxide particles are observed in the atmosphere but they may be also identified in the soils (Strzyszcz, 1983; Magiera *et al*., 2002).

The present results are preliminary and concern the occurrence of the particles of various sizes. In future, investigations of magnetic susceptibility will be carried out to recognize an influence of anthropogenic pollution to the natural environment.

CONCLUSIONS

The particles of the atmospheric dust and the fly ash very often consisted of iron oxides (magnetite, haematite, wüstite and a lot of intermediate phases). The latter ones probably have a different structure, depending on differences in the coal combustion processes. These components comprise average 80–90% wt of all iron oxides particles in the air.

Many of them in the atmosphere have diameters between 5 mm and 10 mm. The results are the preliminary study, which determined the size and distribution of PM5, PM10 and other dust. Due to their size, those particles can be transported for a long distance and they pollute the natural environment. The problem of the environmental protection is especially significant in the highly urbanised areas.

The studies on the iron oxide particles will be continued to determine the influence of these particles on the natural environment especially on the air, soils and a human being.

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