ARCHIVES OF ENVIRONMENTAL PROTECTION

vol. 38 no. 2 pp. 71 - 80 2012

VERSITA

PL ISSN 2083-4772
DOI: 10.2478/v10265-012-0019-3



# MAGNETIC SUSCEPTIBILITY AND HEAVY METAL CONTENT IN DUST FROM THE LIME PLANT AND THE CEMENT PLANT IN OPOLE VOIVODESHIP

BEATA GOŁUCHOWSKA[1]*, ZYGMUNT STRZYSZCZ[2], GRZEGORZ KUSZA[1]

[1]University of Opole, Department of Land Protection, Oleska 22, 45-052 Opole, Poland
[2]Institute of Environmental Engineering of the Polish Academy of Sciences, M. Skłodowskiej-Curie 34, Zabrze, Poland
*Corresponding author's e-mail: beska@uni.opole.pl

**Keywords:** Lime dust, magnetic susceptibility, heavy metals, pH, specific conductivity.

**Abstract:** Until now, dust arising from lime manufacture has been considered harmless to the environment so it has been investigated marginally from the standpoint of environmental protection, especially when it came to magnetic properties and heavy metal content. The aim of the research was filling the gap in this area. The research comprised measurements of magnetic susceptibility, the content of heavy metals, reaction (pH) and specific conductivity of lime dust and also raw material and fuel used for lime production. The samples were taken from one of the lime plants located in Opole Province. Similar investigations were also performed for dust taken from the nearby cement plant using dry method of cement production. It was proven that magnetic susceptibility, heavy metal content and conductivity of lime dust was lower in comparison to cement dust, which resulted from the fact that the lime plant used neither low raw materials nor additives. Due to the high atmosphere dust level in the vicinity of the investigated plants, extremely basic reaction of the tested dust and high content of metals, the studied dust cause alkalization of soils and contribute to the increase of heavy metal content in soils, posing a threat to the environment.

## INTRODUCTION

In recent years, the research into magnetic properties of particulate air pollution coming from various technological processes in terms of their impact on the environment is carried out on an increasingly large scale [1, 5−7, 9, 10, 22, 17]. The intensity and extent of the impact of technogenic dust particles on soils can be assessed by magnetometric method which applies magnetic susceptibility as one of the most useful magnetic parameters in environmental monitoring [8, 11, 12, 15, 18, 19, 21, 23−25].

Until now, the subject of analyses has been mainly dust from power, metallurgical and cement industries, as opposed to the dust arising from the manufacture of lime that has been treated marginally, and there is a gap in this area of study. This gap should be filled, because lime dust may be hazardous to the environment in the areas of high concentration of lime industry, like Opole Voivodeship (Southern Poland).

Lime manufacture is the oldest industrial sector, concentrated in the eastern part of the province of Opole, in the area of three villages: Tarnów Opolski, Górażdże, Gogolin and the town of Strzelce Opolskie. It is connected with high-quality deposits of the Triassic limestone − raw material for the production of lime. At the end of the last century six lime plants were working in the Opole region. Currently there remained two departments belonging to Lhoist SA Lime Plants.

Lime dust has affected soils of Opole Voivodeship for about 500 years. The source of dust was primarily the process of lime burning in shaft furnaces, which had no dust removal devices. These furnaces were operating in lime plants over decades, until the end of the 20th century. For this reason dust coming from shaft furnaces can be regarded as the most important from the standpoint of environmental protection.

Close proximity of cement to lime plants, which use the same raw material deposits, and lack of de-dusting equipment in lime kilns caused significant emissions of dust that might have a significant impact on the quantity and quality of dust falling onto the soil surface.

Although the amount of dust generated in lime kilns was much smaller compared to cement kilns, due to a lower level of dust concentration in off-gases and their lesser volume, the difference in dust emissions was not so significant, because lime kilns − as opposed to cement kilns − were not equipped with any dust-cleaning devices. Lime dust contained less fine grains with a diameter of 0−10 μm (PM10) [16].

According to the archive data, in the 1990s all lime plants of Opole Voivodeship emitted almost as much dust as one cement plant, i.e. about 1000 Mg per year, of which much more than a half came from shaft furnaces. The largest share in air pollution had the lime plant in Górażdże, hence dust coming from this plant is of major importance from the standpoint of environmental impact.

High emissions of dust in the past and their long-term environmental impact were not without effect on soils. This has been confirmed by studies carried out in Opole Voivodeship, which showed that forest soils in the vicinity of cement and lime plants were characterized by increased magnetic susceptibility and heavy metal content [11, 12, 21].

Lime and cement production technologies involve subjecting the raw materials to high-temperature processes, where – as it is known from the literature – ferrimagnetic iron minerals can occur. They are the components of industrial dust and may act as carriers of heavy metals [5, 13, 17]. During lime burning the temperature of charge is high enough (1250–1300°C) to create calcium silicates, aluminates and ferrates, as a result of reactions between oxides of calcium, silicon, aluminum and iron. These minerals decrease the use value of quicklime, therefore – as opposed to the cement production – neither the so called low raw materials nor additives are used in the production of lime, pursuing the lowest content of silicon, aluminum and iron in the burning material.

## CHARACTERISTICS OF THE OBJECTS OF RESEARCH

The main object of the study was the lime plant in Górażdże. It was chosen due to the largest – in comparison to other lime plants – emissions of dust to the atmospheric air, and their long-term impact on the environment reaching the beginning of the sixteenth century. These dusts came mainly from shaft furnaces for lime burning, which did not have any dusting devices.

At the end of the last century, the share of the plant in total dust emissions from the lime industry in Opole Voivodeship was almost 60%, and dust from shaft furnaces accounted for about 70% of emissions, of which 26% constituted the PM10 fraction – much more than in the case of other lime plants [16].

The plant is the production unit of Lhoist SA Lime Plants and its characteristic is based on information obtained in the plant and on the Lhoist SA website. The plant is located about 15 km to the south from the city of Opole, in Górażdże village (Gogolin Municipality). Near the plant (about 2 km to the west) one of the largest cement plants in Europe – Górażdże Cement Plant is located. In the vicinity of both plants, which are surrounded by forests, "St. Anna's Hill" Landscape Park and nature reserves are situated (about 5 km south-east from the lime plant).

The plant exploits the Triassic limestone coming from the górażdżańskie layers of Górażdże deposit, which is also the raw material for clinker production in Górażdże Cement Plant. Burning of lime in the plant on a wide, industrial scale began in the eighteenth century and by the end of the twentieth century was carried out mainly in coke-fired shaft furnaces. In the 60s the plant was equipped with a battery of 5 shaft furnaces of 100B type, with a capacity of 130 Mg lime per day, and an individual department of lime hydration. The coke, coming from nearby Zdzieszowice Coke Plants, was introduced together with the limestone and burned in direct contact with it. Not until the end of the twentieth century, shaft furnaces were liquidated and modern equipment for lime burning was installed: a Maerz regenerative kiln, with a capacity of 600 Mg of lime per day and a Gopex kiln – 350 Mg of lime per day. New kilns are fired with natural gas or coke-oven gas, and the Maerz kiln is equipped with fabric dust collector. This resulted in the reduction of dust emissions to the atmospheric air. The plant produces quicklime in the form of lumps, pieces and powder, as well as hydrated lime and non-burnt products, such as limestone, calcareous aggregate and calcareous flour.

Górażdże Cement Plant belongs to Heidelberg Cement multinational company and is the largest and most modern cement plant in Poland, being in operation for 35 years. The technological process of cement production is composed of two basic steps – clinker baking in rotary kilns and its grinding with additives into cement. At the time of the studies the plant was equipped with two high efficiency rotary kilns, each producing 146 Mg clinker per hour. Currently, after modernization, the efficiency is higher. Cement rotary kilns cooperated with external 4-step cyclone heat exchangers.

The clinker was baked from a mixture containing raw materials: the Triassic limestone from Górażdże deposit and the Cretaceous marl from Opole-Folwark deposit (called "low raw material"). Moreover, various additives were used to produce clinker, e.g. siderite ore siftings and blast furnace sludge from ironworks. Clinker was produced by a dry method. Preparation of a raw material mixture in this method consisted of shredding and drying raw materials, and then grinding them in mills to the form of flour with a water content below 1%. During the time of the studies the plant used hard coal dust as fuel, which was blown into the kilns as a mixture with the air. The cooled clinker with additives such as gypsum and fly ash was ground into cement.

## MATERIALS AND METHODS

The scope of research covered the following topics:

- Collection of dust samples coming from individual stages of lime production process and falling into the area of Górażdże lime plant as well as samples of raw material (limestone) and fuel (coke) used in the production of lime. Besides, in the area of a nearby Górażdże Cement Plant the samples of raw materials used in cement production (limestone and marl), additives, fuel and dustfall were collected.
- Preparation of samples for laboratory analyses (drying, pre-shredding, grinding to the granulation below 200 μm, screening).
- Measurement of pH in $H_2O$ by potentiometric method with a pH-meter N-5170 TELEKO Wrocław and a complex electrode ESAgP-309W EUROSENSOR Gliwice. The instrument was calibrated using buffer solutions of pH 7 and pH 9, due to the alkalinity of most of the investigated materials. Measurements were made after 3 hours from the preparation of the suspension of a 1:1.2 (w/v) dust/water.
- Measurement of specific conductivity (SC) in the suspension of 1:5 (w/v) dust:water, by conductometric method using a conductivity meter with temperature compensation, type CC-317, produced by ELMETRON Zabrze. The apparatus worked with two electrodes: conductometric EPS-2Z and temperature ETP/Pt-100A EUROSENSOR Gliwice. The conductometer was calibrated with standard solution (0.01 N KCl).
- Measurement of volume, low field magnetic susceptibility ($\kappa$) of samples using a Bartington susceptibility meter equipped with a laboratory sensor MS2B, followed by calculation of specific (mass) magnetic susceptibility ($\chi$) by the formula:

$$\chi = \frac{\kappa}{\rho} \tag{1}$$

where: $\chi$ – specific (mass) magnetic susceptibility ($10^{-8}$ $m^3$ $kg^{-1}$),
$\kappa$ – volume, low-field magnetic susceptibility (dimensionless quantity in SI system of units),
$\rho$ – volume density of a sample in natural stage (kg $m^{-3}$).

- Fusion of each sample with sodium carbonate ($Na_2CO_3$), and then dissolution of alloys in concentrated perchloric acid ($HClO_4$) according to Polish standards for cement and lime industry, in order to determine the total content of heavy metals (HM): Cr, Cu, Fe, Mn, Ni, Pb and Zn.
- Determination of the content of Cr, Cu, Fe, Mn, Ni, Pb and Zn by flame-AAS method, using a Perkin-Elmer 1100B spectrometer. The detection limit was 5 mg $kg^{-1}$.
- Dissolution of each sample in hot aqua regia for determination of Cd, Hg and Tl, followed by extraction of these metals from aqueous into organic phase by the MAGIC method [3].
- Determination of Cd, Hg and Tl content by AAS method, using a Perkin-Elmer 6000 spectrometer. For Cd and Hg the detection limit was 0.10 mg $kg^{-1}$, and for Tl 0.50 mg $kg^{-1}$. In some cases, a specific chemical composition of the samples (the so-called matrix effect) caused deterioration of metal detection.

In addition, the amount of each metal introduced into the individual lime kiln together with raw material and fuel per 1 kg of lime was estimated (in mg $kg^{-1}$). Calculations involved the following data: quantity of limestone and coke consumed to produce 1 kg of lime, ignition loss of the coke, the content of HM in limestone, coke and ash after coke combustion. The average consumption rate of the limestone to produce 1 kg of quicklime was 1.9 kg and coke 0.16–0.17 kg, depending on its calorific value.

Afterwards the percentage share of raw material and fuel in the total amount of HM introduced into lime kilns was estimated.

## RESULTS AND DISCUSSION

### *PH and specific conductivity*

The tested lime dust is characterized by pH values in the range of 11.49 (dustfall) to 12.54 (dust from quicklime sorting) (Tab. 1). Dust from the process of quicklime sorting and hydrated lime packing is highly alkaline, but the reaction of the dustfall is slightly lower. This may be caused by the hydration of CaO to $Ca(OH)_2$ and then carbonatization of the resultant $Ca(OH)_2$ with the formation of $CaCO_3$. Taking into account extremely high reaction of the tested dust and high atmosphere dust level in the vicinity of the lime plant in previous years, it can be stated that such dust posed a threat to the environment. Dustfall collected in the area of cement plant was characterized by slightly lower pH values compared to lime dust (Tab. 1).

Table 1. Reaction (pH) and specific conductivity (SC) of raw materials, fuels and dust from the investigated plants

| Description of samples | pH water extract 1:2.5 | SC (µS $cm^{-1}$) water extract 1:5 |
|---|---|---|
| Samples collected in lime plant | | |
| The Triassic limestone | 12.58 | 5650 |
| Coke | 9.26 | 1010 |
| Dust from quicklime sorting department | 12.54 | 7060 |
| Dust from hydrated lime packing department | 12.41 | 4880 |
| Dustfall nr 1 | 11.82 | 650 |
| Dustfall nr 2 – collected under the chimney of shaft furnace | 11.49 | 355 |
| Samples collected in cement plant | | |
| The Triassic limestone | 12.60 | 5340 |
| The Cretaceous marl (low raw material) | 8.50 | 261 |
| Additive nr 1 – siderite ore siftings | 7.86 | 2020 |
| Additive nr 2 – blast furnace sludge | 10.24 | 1116 |
| Additive nr 3 – fly ash | 12.17 | 1870 |
| Coal dust | 8.95 | 455 |
| Dustfall nr 1 | 9.58 | 508 |
| Dustfall nr 2 | 11.77 | 485 |

One of the best known and widely described in the literature effects of the impact of lime and cement dust on the environment is soil alkalization [14, 26]. This is also confirmed by the results of the studies of soils in the vicinity of the lime plant in Górażdże [2]. The studies showed that alkaline deposition on sandy soils resulted in deacidification of the whole level of soil profiles. Alkaline dust caused a rise in reaction (pH values) of soil pits in all transects of studies (western W, northwestern NW and southwestern SW). Investigated pits were characterized by the rise in reaction by 3−4 pH units in the case of forest stands and 1−2 units for meadows, arable soils and wastelands. Emission of lime dust changed soil reaction into the neutral and alkaline. This applies particularly to the top levels of soils (detritus, turfy) and the humus level, which were the most affected by alkaline deposition. Alkaline falling dust enriched the tested soil pits in calcium carbonate, mainly those located in close proximity to the lime plant, where above 1% of $CaCO_3$ was found.

The problem of transformation of soils and plant communities influenced by alkaline dust deposition from cement and lime plants was widely described by A. Świercz [26] who studied the impact of cement and lime emissions on forest ecosystems in White Basin (Świętokrzyskie Voivodeship, South-East Poland). The author has found a strong alkalization of forest soils, expressed, among others, as changes in soil buffering and the content of elements in soils, such as Ca, Mg, Mn, Al, and Fe, accompanied by the transformation of plant communities.

Specific conductivity of the tested lime dust varied from 355 (dustfall) to 7060 $\mu S\ cm^{-1}$ (dust from quicklime sorting) (Tab. 1). Dust arising from the mechanical processing of quicklime contains more soluble salts than the raw material (limestone). The falling dust is characterized by much smaller SC than the dust from the sorting and packing of lime. In the case of a nearby cement plant, the values obtained for the falling dust are within the range recorded for the lime plant.

The results of conductivity measurements of soils in the vicinity of the lime plant in Górażdże proved that the salinity of investigated soil levels was influenced by alkaline emissions to much lesser extent than reaction and the content of calcium carbonate. The investigated soil samples were characterized by low SC values well below 1000 $\mu S\ cm^{-1}$ [2].

### *Magnetic susceptibility and heavy metals*

Magnetic susceptibility of the tested lime dust ranged from 7 (dust from quicklime sorting) to $52 \times 10^{-8}\ m^3kg^{-1}$ (dust from hydrated lime packing) (Tab. 2). Low values of magnetic susceptibility prove that weakly magnetic iron (paramagnetic, antiferromagnetic) prevailed in the tested dust samples. Despite this fact, magnetic properties of the dust were probably affected by ferrimagnetic minerals, since in most samples magnetic susceptibility exceeded the value of $10 \times 10^{-8}\ m^3kg^{-1}$ [4].

The results indicate that raw material (limestone) had greater impact on the content of heavy metals in dust emitted from lime kilns, which affected soils during centuries, than the fuel (coke). Limestone was found as the main source of Cr, Cu, Fe, Mn, Ni, Pb and Zn in lime kilns, and its share in the total amount of these metals introduced into the kilns changed from 79.8 to 98.3% (Tab. 3). Compared to the limestone, ash from coke combustion in shaft furnaces could have a significant impact on magnetic susceptibility of the falling dust.

Table 2. Magnetic susceptibility (χ) and the total content of iron (Fe) in raw materials, fuels and dust from the investigated plants

| Description of samples | χ ($\times 10^{-8}$ $m^3$ $kg^{-1}$) | Fe (mg $kg^{-1}$) |
|---|---|---|
| Samples collected in lime plant | | |
| The Triassic limestone | 2 | 1760 |
| Coke | 55 | 52825* |
| Dust from quicklime sorting department | 7 | 3205 |
| Dust from hydrated lime packing department | 52 | 2910 |
| Dustfall nr 1 | 37 | 3565 |
| Dustfall nr 2 – collected under the chimney of shaft furnace | 22 | 3220 |
| Samples collected in cement plant | | |
| The Triassic limestone (high raw material) | 2 | 1285 |
| The Cretaceous marl (low raw material) | 3 | 7485 |
| Additive nr 1 – siderite ore siftings | 95 | 174895 |
| Additive nr 2 – blast furnace sludge | 6641 | 334395 |
| Additive nr 3 – fly ash | 938 | 43800 |
| Coal dust | 3 | 57350* |
| Dustfall nr 1 | 221 | 14700 |
| Dustfall nr 2 | 241 | 28300 |

Explanation:
* – ash analysis

Table 3. Percentage share of heavy metals (HM) introduced into shaft furnaces in the lime plant together with raw material and fuel

| Description of samples | HM (% w/w) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Fe | Cr | Zn | Cd | Mn | Cu | Ni | Pb | Hg | Tl |
| Limestone | 79.8 | 88.4 | 97.5 | < 98.5 | 96.3 | 95.0 | 98.3 | 95.1 | < 91.3 | < 91.8 |
| Coke* | 20.2 | 11.6 | 2.5 | < 1.5 | 3.7 | 5.0 | 1.7 | 4.9 | < 8.7 | < 8.2 |

Explanation:
* – ash analysis

The dustfall from the area of the lime plant was characterized by significantly lower MS values and HM content than from the cement plant (Tab. 2, Tab. 4). This concerned all tested metals, but especially Cr, Fe, Mn, Zn, Cd and Tl. The decrease in MS and HM content in the dustfall may be related to the fact that neither so called “low raw materials”, such as marl, nor additives, such as metallurgical waste, fly ash, iron ore processing waste were used in the process of lime production (Tab. 4). It probably resulted in the decrease in ferrimagnetic minerals and heavy metals amount introduced into the lime kilns and

Table 4. The content of heavy metals (HM) in raw materials, fuels and dust from the investigated plants

| Description of samples | HM (mg kg$^{-1}$) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Cr[1] | Cd[2] | Zn[1] | Mn[1] | Cu[1] | Ni[1] | Pb[1] | Hg[2] | Tl[2] | Fe[1] |
| Samples collected in lime plant | | | | | | | | | | |
| The Triassic limestone | 20 | 0,62 | 65 | 115 | 50 | 160 | 90 | <0,10 | <0,50 | 1760 |
| Coke* | 315 | <0,11 | 200 | 525 | 315 | 340 | 550 | <0,11 | <0,53 | 52825 |
| Dustfall nr 1 | 30 | 1,19 | 170 | 135 | 120 | 165 | 290 | 0,14 | <0,68 | 3565 |
| Samples collected in cement plant | | | | | | | | | | |
| The Triassic limestone (high raw material) | 15 | 0.63 | 65 | 85 | 45 | 145 | 130 | <0.10 | <0.50 | 1285 |
| The Cretaceous marl (low raw material) | 25 | 0.12 | 40 | 135 | 40 | 160 | 65 | <0.12 | <0.58 | 7485 |
| Additive nr 1 – siderite ore siftings | 105 | 0.43 | 220 | 3100 | 90 | 220 | 235 | <0.12 | 0.65 | 174895 |
| Additive nr 2 – blast furnace sludge | 95 | 29.60 | 7000 | 2100 | 125 | 170 | 1750 | 0.24 | 4.41 | 334395 |
| Additive nr 3 – fly ash | 170 | nd | 340 | 595 | 105 | 300 | 395 | nd | nd | 43800 |
| Coal dust* | 150 | 0.16 | 545 | 1005 | 175 | 320 | 460 | <0.14 | <0.71 | 57350 |
| Dustfall nr 1 | 60 | nd | 595 | 295 | 310 | 180 | 475 | nd | nd | 14700 |
| Dustfall nr 2 | 125 | 2,71 | 1250 | 305 | 170 | 70 | 245 | 0,32 | 7,25 | 28300 |

Explanations:
[1] – total amount; [2] – fraction dissolvable in aqua regia; * – ash analysis; nd – not determined

lime mills which led to the reduction in the amount of these components in emitted and falling dust.

This was confirmed by the analyses of additives used in cement production which were characterized by much higher values of MS and HM content in comparison to the limestone being the basic raw material. Among the additives, the highest content of highly hazardous metals, such as Cd, Zn, Pb, Hg and Tl, was noted in blast furnace sludge – the waste form metallurgy.

Taking into account the content of heavy metals in falling dust samples, the atmosphere dust level at which the precipitation of the investigated metals exceeded the applicable Polish protection standards was calculated [20]. The results were compared to the archive data provided by Górażdże Cement SA on dust precipitation, which in the vicinity of the lime plant varied from 67.1 to 440.9 g m$^{-2}$ per year. The values were higher than in the area of Górażdże Cement Plant (51.1–355.0 g m$^{-2}$ per year). The calculations showed that at such level of atmospheric pollution, the precipitation of lead exceeded the protective standard of 100 mg m$^{-2}$ per year, but decrease in amount of falling dust to the level of 200 g m$^{2}$ per year would result in decrease of lead precipitation to the level not creating a danger.

In the case of cement plant the situation is different, since at the level of atmospheric pollution noted in the area of this plant, precipitation of 4 metals (Zn, Mn, Cu and Pb) might have been exceeded. As follows from the calculations, the excessive precipitation of these metals could take place even when the amount of falling dust was less than the accepted standard value 200 g $m^2$ per year. The results indicate that reduction in the degree of atmospheric dust level to standard protection level accepted in Poland, does not always solve the problem of air pollution with metals. Reduction in the content of metals in emitted dust is of crucial importance.

## CONCLUSIONS

1. The study showed that lime dust is characterized by particular magnetic susceptibility values and heavy metal content, depending on a much smaller number of factors compared to other technogenic dust, coming from high-temperature processes, like cement production.
2. Magnetic susceptibility and heavy metal content in the tested lime dust was lower in comparison to cement dust, which resulted from the fact that neither low raw materials nor additives were used in the production of lime. This also applies to the specific conductivity values of the examined dust.
3. Large amount of dust falling onto the soil surface in the area of the investigated plants in the past meant that they were hazardous to the environment and human health because of excessive content of metals.
4. Extremely high reaction of the tested dust results in chemical transformation of soils in the vicinity of the investigated plants. It requires further, continuous, detailed monitoring of soil processes and transformation of vegetation cover in this area.

## REFERENCES

[1] Blaha U., B. Sapkota, E. Appel, H. Stanjek, W. Rösler: *Micro-scale grain-size analysis and magnetic properties of coal-fired power plant ash and its relevance for environmental magnetic pollution studies*, Atmospheric Environment, **42**, 8359−8370 (2008).

[2] Bruchal M.: *Wpływ zakładów wapienniczych na odczyn gleb terenów przyległych*, praca magisterska maszynopis, Katedra Ochrony Powierzchni Ziemi, Uniwersytet Opolski, Opole 2010.

[3] Clark J.R., J.G. Viets: *Multielement extraction system for the determination of 18 trace elements in geochemical samples*, Analytical Chemistry, **53 (1)**, 61–65 (1981).

[4] Dearing J.: *Environmental magnetic susceptibility, Using the Bartington MS2 System*, Chi Publishing, Kenilworth, England, 1999.

[5] Gołuchowska B.J.: *Some factors affecting an increase in magnetic susceptibility of cement dust*, Journal of Applied Geophysics, **48 (2)**, 103−112 (2001).

[6] Gołuchowska B., Z. Strzyszcz: *Wpływ technologii produkcji klinkieru na zawartość metali ciężkich w pyłach powstających w procesie jego wypalania*, Chemia i Inżynieria Ekologiczna, **6 (2−3)**, 217−227 (1999).

[7] Jabłońska M., D. Smołka-Danielowska: *Iron oxides particles in the air and fly ash, and their influence on the environment (preliminary studies)*, Polish Geological Institute, Special Papers, **24**, 93−98 (2008).

[8] Kapička A., N. Jordanova, E. Petrovský, V. Podrazský: *Magnetic study of weakly contaminated forest soils*, Water Air and Soil Pollution, **148 (14)**, 31−44 (2003).

[9] Konieczyński J., B. Komosiński, M. Zelechower: *Properties of particulate matter emitted from manufacturing of ceramic products*, Archives of Environmental Protection, **33 (2)**, 3−22 (2007).

[10] Konieczyński J, K. Stec : *The occurrence of selected trace elements in grain fractions of dust emitted from power, coke and cement plants*, Archives of Environmental Protection, **35 (4)**, 3−21 (2009).

[11] Kusza G., Z. Strzyszcz: *Forest reserves of Opole Province – state and technogenic hazard*, Institute of Environmental Engineering of the Polish Academy of Sciences, Works and Studies, **63**, Zabrze, 1−156 (2005a).

[12] Kusza G., Z. Strzyszcz: *Podatność magnetyczna gleb w niektórych rezerwatach leśnych Opolszczyzny*, Monografie Komitetu Inżynierii Środowiska PAN **2 (33)**, 587−594 (2005b).
[13] Lauf R.J., A.H. Lawrence, S.S. Rawiston: *Pyrite framboids as the source of magnetite spheres in fly ash*, Environmental Science and Technology, **16**, 218–220 (1982).
[14] Jakubczak Z., Z. Adamczyk-Winiarska, J. Gądor: *Ilość i skład chemiczny pyłów opadających w rejonie Kombinatu Cementowo-Wapienniczego „Nowiny"*, Pamiętnik Puławski – Prace IUNG, **87**, 171–185 (1986).
[15] Petrovský E., B. B. Ellwood: *Magnetic monitoring of air-, land-, and water-pollution*, [in:] B. A. Maher, R. Thompson (eds.), *Quaternary Climates Environments and Magnetism*, Cambridge Univ. Press, 279−322 (1999).
[16] Rybarczyk A.: *Ocena oddziaływania przemysłu cementowo-wapienniczego województwa opolskiego na stan środowiska przyrodniczego – stan aktualny oraz postulowane kierunki zmian*, Instytut Mineralnych Materiałów Budowlanych, PW 176/UW, Opole (1994).
[17] Magiera T., M. Jabłońska, Z. Strzyszcz, M. Rachwał: *Morphological and mineralogical forms of technogenic magnetic particles in industrial dusts*, Atmospheric Environment, **45**, 4281−4290 (2011).
[18] Magiera T., Z. Strzyszcz, M. Rachwał: *Magnetic susceptibility of forest topsoils in mountains regions of southern Poland based on fields measurement techniques*, Polish Journal of Soil Science, **39 (2)**, 101−108 (2006).
[19] Magiera T., Z. Strzyszcz, M. Rachwał: *Mapping particulate pollution loads using soil magnetometry in urban forests in the Upper Silesia Industrial Region*, Poland, Forest Ecology and Management, **248**, 36–42 (2007).
[20] Rozporządzenie Ministra Środowiska z dnia 26 stycznia 2010 r. w sprawie wartości odniesienia dla niektórych substancji w powietrzu, Dziennik Ustaw z dnia 3 lutego 2010 r., Nr 16, poz. 87, zał. 1, tab. 2.
[21] Strzyszcz, Z.: *Gehalt an Ferromagnetika in den von der Immision der Zementindustrie in der Wojewodschaft Opole beeinflussten Böden*, Mitteilungen der Bodenkundlichen Gesellschafft, **76**, 1477−1480 (1995).
[22] Strzyszcz Z., T. Magiera: *Podatność magnetyczna niektórych przemysłowych pyłów atmosferycznych i jej znaczenie w monitoringu ekologicznym powierzchni ziemi*, Instytut Podstaw Inżynierii Środowiska PAN, Prace i Studia, **54**, 205−215 (2000).
[23] Strzyszcz, Z., T. Magiera, F. Heller: *The influence of industrial emissions on the magnetic susceptibility of soils in Upper Silesia*, Studia geophysica et geodaetica, **40**, 276−286 (1996).
[24] Strzyszcz Z., T. Magiera, M. Rachwał: *Application of soil magnetometry for identification of technogenic anomalies of trace metals and iron contents: a case study in the Katowice Forest District*, Polish Journal Environmental Study, **15 (2a)**, 176−184 (2006).
[25] Strzyszcz Z., M. Rachwał: *Changes in magnetic susceptibility of forest soils along the west and south border of Poland*, Archives of Environmental Protection, **34 (1)**, 71−79 (2008).
[26] Świercz A.: *Analiza procesów glebowych i przekształceń roślinnych w zalkalizowanych siedliskach leśnych region świętokrzyskiego*, Polska Akademia Nauk, Komitet „Człowiek i Środowisko" przy Prezydium PAN, Zeszyty Naukowe **39**, Warszawa−Kielce (2005).

## PODATNOŚĆ MAGNETYCZNA I ZAWARTOŚĆ METALI CIĘŻKICH W PYŁACH Z ZAKŁADU WAPIENNICZEGO W WOJEWÓDZTWIE OPOLSKIM

Pyły powstające przy produkcji wapna uważane były za nieszkodliwe dla środowiska i w związku z tym były one badane marginalnie, szczególnie jeśli chodzi o właściwości magnetyczne i zawartość metali ciężkich. Celem prezentowanych badań było uzupełnienie luki w tym zakresie. Badania obejmowały pomiary podatności magnetycznej oraz oznaczenia zawartości metali ciężkich, pH i przewodnictwa właściwego pyłów wapienniczych, a także surowca i paliwa, używanego do produkcji wapna. Próbki zostały pobrane w jednym z zakładów wapienniczych województwa opolskiego. Podobne badania wykonano także dla pyłów pobranych w pobliskiej cementowni stosującej suchą metodę produkcji cementu. Wykazano, że podatność magnetyczna, zawartość metali ciężkich i przewodnictwo właściwe pyłów wapienniczych jest niższe w porównaniu do cementowych, co wynikało z faktu, że zakład wapienniczy nie stosował surowców niskich ani dodatków. Z powodu dużego opadu pyłu w rejonie badanego zakładu oraz bardzo wysokiego odczynu pyłów wapienniczych, mogą one powodować alkalizację gleb i przyczyniać się do wzrostu zawartości w nich metali ciężkich, stwarzając zagrożenie dla środowiska.