

Beata J. GOŁUCHOWSKA¹ and Grzegorz KUSZA¹

LIME DUSTS AS A SOURCE OF ENVIRONMENTAL POLLUTION IN OPOLE PROVINCE

PYŁY WAPIENNICZE ŹRÓDŁEM ZANIECZYSZCZEŃ ŚRODOWISKA W WOJEWÓDZTWIE OPOLSKIM

Abstract: Until now dusts arising from lime manufacture have been considered harmless to the environment so they have 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 ferrimagnetic minerals, heavy metals, reaction (pH) and conductivity of the dust and also the raw material and fuel used for lime production. The samples were taken from the lime plant located in the Opole province. Similar investigations were also performed for dusts taken from the nearby cement plant using dry method of cement production. It was proven that magnetic susceptibility, heavy metal content and conductivity of the lime dusts was lower in comparison to the cement dusts, which resulted from the fact that the lime plant used neither so called low raw materials (like marl or clay) nor additives. Due to the high atmosphere dust level in the vicinity of the lime plant and extremely basic reaction of lime dusts, they may cause alkalization of soils and contribute to the increase of heavy metal content in soils, posing a threat to the environment.

Keywords: lime dust, magnetic susceptibility, heavy metal content, pH, conductivity

In recent years, on an increasingly larger scale the research into magnetic properties of particulate air pollution coming from the various technological processes is carried out, in terms of their impact on soils [1-3]. From the standpoint of environmental protection one of the most useful magnetic parameters is magnetic susceptibility and its application to assess the intensity and extent of the impact of technogenic dust particles on soils. Until now the subjects of the analyses were mainly dusts from power, metallurgical and cement industry, as opposed to the dusts arising from the manufacture of lime that has been treated marginally, and there is a gap in this area of study [4]. Moreover, the close proximity of cement to lime plants, which use the same raw material deposits, and lack of dedusting equipment in lime kilns causes significant emissions of particulate matter that may have a significant impact on the quantity and quality of dusts falling onto the soil [5, 6]. It has been supported by the studies done in the Opole province, which showed that soils in the vicinity of cement and lime plants were characterized by increased magnetic susceptibility and heavy metal content [7].

Over a span of the research the Gorazdze Production Division occupied the first place in the region in terms of hydrated lime production volume. Besides, the plant produced quicklime in lumps and soil lime (calcium oxide fertilizer). The most important and most dusting technological operation in the production of lime was its burning. The plant used the Triassic limestone as a raw material coming from the gorazdzanskie layers of the Gorazdze deposit, which was also exploited by the Gorazdze Cement Plant to produce clinker. Raw material was prepared in advance in sorting and breaking department of the Gorazdze Mine. Lime burning took place in the coke-fired shaft furnaces.

¹ Independent Department of Land Protection, Faculty of Natural Science and Technology, University of Opole, ul. Oleska 22, 45-052 Opole, tel. 77 401 60 20, fax 77 401 60 30, email: beska@uni.opole.pl, Grzegorz.Kusza@uni.opole.pl, kopz@uni.opole.pl

The range and methods of research

The scope of research covered the following topics:

- Raw material (limestone) and fuel (coke) sampling, being used in lime production, as well as dusts coming from the production process and falling in the area of the plant.
- Physicochemical analyses: measurement of reaction (pH) by potentiometric method and conductivity (SC) by conductometric method.
- Magnetic analyses: measurement of magnetic susceptibility (χ) by means of MS2B Bartington susceptibility bridge, determination of ferrimagnetic minerals (FM) content by Forgenta FMA 5000 analyser.
- Determination of the content of heavy metals (HM) by AAS method, by means of the Perkin-Elmer 1100B spectrometer in the case of Cr, Zn, Mn, Cu, Ni, Pb and Fe, and the Perkin-Elmer 6000 for Cd, Hg and Tl.

The above investigations were also performed for the dustfall taken from the nearby Gorazdze Cement Plant. Based on the results of FM content in the samples, and Fe in the model magnetite, the amount of iron forming these minerals was estimated. It has been called ferrimagnetic iron and marked with the symbol Fe*. Then the ratio of Fe to Fe* was estimated, where Fe stands for the total iron. In this way the information was obtained which part of the total iron is strongly magnetic in character.

Results and discussion

Reaction (pH) and conductivity

The investigated lime dusts are characterized by pH values in the range of 11.49 (dustfall) to 12.54 (dust from quicklime sorting) (Table 1).

Table 1
The pH, (specific) conductivity (SC), magnetic susceptibility (χ), the content of ferrimagnetic minerals (FM), ferrimagnetic iron (Fe*) and the total iron (Fe) in raw material, fuel and dusts from the Gorazdze Production Division

Description of the samples	pH water extract 1:2.5	SC [$\mu\text{S cm}^{-1}$] water extract 1:5	χ [$10^{-8} \text{ m}^3 \text{ kg}^{-1}$]	FM [% by weight]	Fe* [mg kg^{-1}]	Fe [mg kg^{-1}]	Fe*/Fe [% by weight]
Limestone	12.58	5650	26	0.01	71	1760	4.0
Coke	9.26	1010	81	0.16	1133	52825 ^{x/}	-
Dust from the quicklime sorting department	12.54	7060	40	0.05	354	3205	11.0
Dust from the hydrated lime packing department	12.41	4880	74	0.14	991	2910	34.1
Dustfall nr 1	11.82	650	58	0.10	708	3565	19.9
Dustfall nr 2	11.49	355	50	0.08	566	3220	17.6
Dustfall from the Gorazdze Cement Plant	11.77	485	276	0.68	4814	28300	17.0

Explanation: x/ - ash analysis

The dusts from sorting of quicklime and packing of hydrated lime are highly alkaline, and the reaction of the dustfall is somewhat lower (alkaline). This may be caused by the hydration of CaO, and then the carbonatization of the resultant Ca(OH)₂ with the formation of CaCO₃. Due to the extremely high reaction lime dusts pose a threat to the environment. One of the best known and widely described in the literature results of the impact of such dusts on the environment is alkalization of soils [8, 9].

SC of the dusts collected in the investigated plant varies from 355 (dustfall) to 7060 $\mu\text{S cm}^{-1}$ (dust from quicklime sorting). The dust arising from the mechanical processing of quicklime (crumbling) contains more soluble salts than the raw material (limestone). The falling dust is characterized by much smaller SC than the dusts from the sorting and packing of lime. In the case of the Gorazdze Cement Plant the values obtained for the falling dust are within the range recorded for the lime plant.

Table 2
Heavy metal (HM) contents in raw material, fuel and dustfall from the Gorazdze Production Division

Description of the 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/}
Limestone	20	0.62	65	115	50	160	90	<0.10	<0.50	1760
Coke ^{x/}	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
Dustfall from the Gorazdze Cement Plant	125	2.71	1250	305	170	70	245	0.32	7.25	28300

Explanations: 1/ - total amount, 2/ - fraction dissolvable in *aqua regia*, x/ - ash analysis

Magnetic susceptibility, ferrimagnetic minerals and heavy metals

The results indicate that the contents of HM in lime dusts is influenced by the raw material and fuel used in the manufacture of lime. The main source of Cr, Zn, Mn, Cu, Ni, Pb and Fe in shaft furnaces was the raw material - limestone, and therefore it could have the greater impact on the content of HM in the falling dusts, than the fuel. The share of raw material in the total amount of Cr, Zn, Mn, Cu, Ni, Pb and Fe being introduced into the shaft furnaces changed from 79.8 to 98.3%.

Alongside with the coke into the shaft furnaces was introduced more FM (57.8%) and Fe (20.2%) than the other investigated heavy metals (from 1.7 to 11.6%), with the result that the fuel could have a significant impact on MS and Fe content in the falling dusts. The dustfall in the lime plant area was characterized by significantly lower χ and HM content than the dustfall in the cement plant (Tables 1, 2). This concerned mainly Cr, Zn, Mn, Cu, Pb, Tl and Fe and - to a lesser extent - Cd, Ni and Hg. Reduction of χ and HM content in the dustfall from the lime plant may be related to the fact that neither so called low raw materials, like marl, nor additives were used in the production of lime. In addition, the lime plant did not add fly ashes, gypsum rock, or other additives to lime during its milling, which could cause that a smaller amount of FM and HM, especially Cr, Mn, Cu and Fe, was introduced into the lime mills in comparison with the cement mills in the cement plant.

Entering FM and HM into the shaft furnaces and lime mills in a reduced quantity could lead to the reduction of their content in the dusts raised from these devices as well as the falling dusts.

Taking account of the content of HM in falling dusts, the atmosphere dust level at which the precipitation of the investigated metals exceeded the applicable protection standards was calculated [10]. The results were compared to the actual dust precipitation, which values in the vicinity of the lime plant varied from 67.1 to 440.9 g m⁻² per year and were higher than in the area of the Gorazdze Cement Plant (51.1÷355.0 g m⁻² per year, according to the data of the Gorazdze Cement and Lime Plants for Chorula village). It is known from the calculations, that at such level of atmospheric pollution, the precipitation of Pb could exceed the adopted protective standard, but the reduction in the amount of the dustfall to the level of 200 g m² per year would result in the decrease of Pb precipitation to the level not creating a danger.

Conclusions

1. Magnetic susceptibility and heavy metal content in dusts coming from the shaft furnaces in lime plants depends on the type of raw materials and fuels used for lime manufacture, and the size of their consumption. The richer in ferrimagnetic minerals and heavy metals are the raw materials and fuels, and the more of them is needed to produce 1 Mg of lime, the greater magnetic susceptibility and heavy metal content in the dusts.
2. A large amount of dusts falling in the area of the investigated lime plant meant that they could be dangerous to the environment because of excessive lead content.
3. Magnetic susceptibility and heavy metal content in dusts from the lime plant was lower in comparison to the cement dusts, which resulted from the fact that neither low raw materials nor additives were used in the lime plant. This also applies to the conductivity of the dusts.

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PYŁY WAPIENNICZE ŹRÓDŁEM ZANIECZYSZCZEŃ ŚRODOWISKA W WOJEWÓDZTWIE OPOLSKIM

Samodzielna Katedra Ochrony Powierzchni Ziemi, Uniwersytet Opolski

Abstrakt: Pyły powstające przy produkcji wapna uważano 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, zawartości minerałów ferrimagnetycznych, metali ciężkich, pH i konduktywność 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 konduktywność pyłów wapienniczych są mniejsze w porównaniu do pyłów cementowych, co wynikało z faktu, że zakład wapienniczy nie stosował tzw. surowców niskich, jak margle i ility, ani dodatków. Z powodu dużego opadu pyłu w rejonie badanego zakładu wapienniczego oraz bardzo dużej wartości pH pyłów wapienniczych mogą one powodować alkalizację gleb i przyczyniać się do wzrostu zawartości w nich metali ciężkich, stwarzając zagrożenie dla środowiska.

Słowa kluczowe: pyły wapiennicze, podatność magnetyczna, zawartość metali ciężkich, pH, przewodność