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EMISSION OF POLYCYCLIC AROMATIC HYDROCARBONS FROM THE EXHALATION ZONES OF THERMALLY ACTIVE MINE WASTE DUMPS

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Abstract
The article presents results of research carried out on the occurrence of polycyclic aromatic hydrocarbons (PAH) in gases of exhalation zones, created on the surface of a thermally active coal mine waste dump. The oxidation and self-heating of mine waste are accompanied with the intensive emission of flue gases, including PAH group compounds. Taking into consideration the fact the hydrocarbons show strong genotoxic, mutagenic and carcinogenic properties, research was conducted to establish their content in the examined gases. The research object was a gangue dump located in Rybnik. The research was performed in 2012. In total, 24 samples of gas were collected with PUF (polyurethane foam) sampling cartridges with a quartz fibre filter and an aspirator. The collected samples were analysed with the use of high performance liquid chromatography (HPLC) and a fluorescence detector (FLD) to evaluate the amount of PAH present.

Keywords
polycyclic aromatic hydrocarbons (PAH), thermally active coal gangue dump, exhalation zones

1. INTRODUCTION

The Upper Silesian Industrial Region, being one of the most urbanized and industrialized areas of Europe, is an example of significant changes to terrain resulting from coal mining. Symptoms of the changes are anthropogenic forms of terrain – mine waste dumps, colloquially called, among others, tailing heaps. Specific conditions of coal production in Poland have resulted in, over the last several decades, the extraction of large amounts of gangue rocks. The deposited waste material contains coal, bands of coal, coal shale and other incidental combustible materials. According to various sources, it is estimated that for each 1 Mg of coal produced, there is 0.4–0.5 Mg of waste material (Gumińska, Różański 2005; Korban 2011), which has to deposited in the dumps. According to data from the Central Statistics Office (Główny Urząd Statystyczny), 76.5 million Mg of coal was produced in Poland in 2011 (www.stat.gov.pl). This means that approximately 30.6–38.3 million Mg of waste material was produced in the year as well.

In the past, due to technical limitations and poorly developed methods of waste management, the vast majority of this waste material was stored in a haphazard fashion on the surface in tips or dumps. The lack of waste segregation, mixing (Czuber, Duchowski 1979) or compacting, as well as ignoring rules regarding fire prevention (Pikoń, Bugla 2007) are nowadays a cause of numerous spontaneous combustion events in several-decade-old mine waste dumps. Coal substance and pyrite present in waste material undergo intensive oxidization, which leads to self-heating inside the dump.

In these conditions, favourable for thermal phenomena, the temperature rises significantly, as a consequence it can lead to dump fires (Korski 2010). The development of new methods of waste management have resulted in a decrease in the material being deposited in dumps. At the same time, preventive measures limit the possibilities of fires occurring. Yet the problem of fires in coal mine waste dumps still remains present, as well as the issue of toxic gas emissions from mine waste dumps to the atmosphere, which are the subject of numerous publications (e.g. Falcon 1986; Adamczyk, Białecka 1999; Konopacki 2007).

Coal mine waste dumps are often thermally active, i.e. the temperature on their surface, inside them and in the cracks occurring on the surface, is very high. The cracks emit different kinds of toxic gases (Hławiczka, Łączny 1987; Buchta, Molenda 2007). Thermal activity is observed mainly in the old sites and in the relatively new ones too, where fire prevention has not been sufficient. The vast surface they cover and their vicinity to inhabited areas makes them burdensome. A burning coal mine dump, with time, may adversely affect its surroundings due to spreading the fire and the resulting air pollution (Czuber, Duchowski 1979).

In the Silesian Voivodeship there are 136 coal mine waste dumps (Misz, Fabiańska, Ćmiel 2007; Różański, Parchański 2009), 15 of them are thermally active ones (Projekt COOL'S 2007–2013). They are located in the central part of the Upper Silesian Coal Basin, i.e. near Ruda Śląska, Zabrze and the Rybnik Coal Area. The research object was one of the mine waste dumps located in Rybnik, reclaimed between 1994 and 1999, where thermal phenomena started again in 2001. Cracks emitting vaporous gases were observed there and have formed so-called exhalation zones (Photo 1) which are anthropogenic counterparts of volcanic solfataras (Buchta, Molenda 2007). The following article presents results of analyses performed in 2012. Their aim was to establish the content of polycyclic aromatic hydrocarbons (PAH) in the gases generated there.

Photo 1. Example of an exhalation zone (Photo by P. Kuna)

Because of the genotoxic, mutagenic and carcinogenic properties of PAH compounds, as well as a lack of literature reference concerning mine waste dump fires and their influence on the environment; it seems justified to conduct the research. On one hand, it is an attempt to fill up the gaps in the given research area (as the issue of PAH occurrence in the gases emitted in burning mine waste dumps requires detailed studies). On the other hand, it is an answer to the postulates of the U.S. Environmental Protection Agency (1999), which, taking into consideration the strong genotoxic, mutagenic and carcinogenic properties of hydrocarbons; advises controlling their levels in the main elements of the environment e.g. water, soil and air. The compounds, present in the air, may transform when reacting with other hydrocarbons, or other substances emitted in burning mine waste dumps, e.g. sulphur dioxide, nitrogen oxides, carbon oxide and hydrogen sulfide (Krogulski, Borkowska, Strusiński 1997). As a result of the transformations, substances of increased or decreased mutagenic activity or toxicity may be created. Determining the concentration levels of the pollutants is important for the proper assessment of the environmental threat they may pose, and for the local community.

2. CHARACTERISTICS OF BURNING COAL MINE WASTE DUMPS

2.1. Phenomenon of spontaneous combustion of mine waste

The problems associated with thermal activity concern only a certain specific group of mine waste dumps i.e. coal mine waste (Dulewski, Madej, Uzarowicz 2010). Coal mine waste can have quite variable content, usually including claystone, mudstone, sandstone and coal shale (Misz-Kennan, Fabiańska 2010). According to Różański and Parchański (2009), the share of the main combustible material in coal mine waste deposited in dumps may reach even 30% for coal substance and 8% for pyrite.

Buchta and Molenda (2007) claim that fire resulting from waste materials deposited in dumps may be the result of two kinds of processes:

- exogenic processes, where the source of heat is external
- endogenic processes, occurring as a result of low-temperature oxidation of coal and pyrite, in relation to the amount of available oxygen, characterised by massive emissions of heat

It should be emphasised that the mechanism regarding the occurrence of endogenic fires is a complex phenomenon that has not yet been fully explained. There are several theories concerning the factors that can activate the spontaneous combustion of coal. The more significant theories are as follows: pyrite theory, catalytically bacterial theory, peroxide theory and phenol theory. Figure 1 shows the schematics of factors which can start mine waste dump fires.

2.2. Creation of exhalation zones in thermally active mine waste dumps

The amount of coal in waste material is one of the factors that can trigger a fire or promote its development. Coal may be present in the form of lumps, bands or organic substance dispersed/scattered in the rocks. Other factors supporting or limiting the occurrence of fires are the methods and technology used when depositing waste material, and its compaction ratio in the dump. Waste materials of low compaction are more prone to spontaneous combustion, because air and water penetrate them more easily (effective porosity of a dump). Consequently, intensive weathering and oxidizing processes take place within/inside a dump. Moreover, low compaction and the shape of a dump can facilitate convection inside which, in turn, promotes spontaneous combustion. A more frequent occurrence of the phenomenon in zones close to the surface of dumps confirms this (Fig. 2). The concurrence of several causes promoting spontaneous combustion, as well as exothermal reactions accompanying bacterial and chemical activity during the oxidation of pyrite, increases temperature inside the dump. All these factors promote the convection of air and water vapour within a dump. This, in turn, accelerates the oxidation of pyrite and supports bacterial activity, increasing the thermal activity even further, leading to endogenous fires. In spite of the fact that the fire terminates bacterial activity, the process still continues leading to fires in other areas of the dump. Further development depends on the availability of oxygen within the dump and the amount of coal in the waste material.

The chemical composition of products created during the fire depends on the temperature within its centre, the mineral and chemical composition of the waste material (coal, hydrogen, sulphur, sodium, chlorine, iron and calcium), as well as the amount of available water and oxygen. Sodium, chlorine, iron and calcium support thermal transformations of minerals, playing a role of a kind of flux for the burning mine waste materials. Fluxes, while lowering the temperature of melting, at the same time accelerate the process of burning carboniferous rocks, lowering the need for energy necessary for thermal transformations. Briefly, the elements are catalysts of high-temperature transformations within the dump. Volatile products of thermal transformations of rocks enter reactions with flue gases and water vapour, changing the composition of the resulting gases. Because of the thermal transformations within the dump, the volume of deposited waste material decreases. Consequently, cracks and crevasses appear on the surface. They, in turn, will become the preferred exhalation zones of flue gases. Moreover, the process of melting mine waste materials leads to creating new mineral forms – mainly silicates and aluminosilicates, iron, calcium, sodium and potassium (Photo 2).

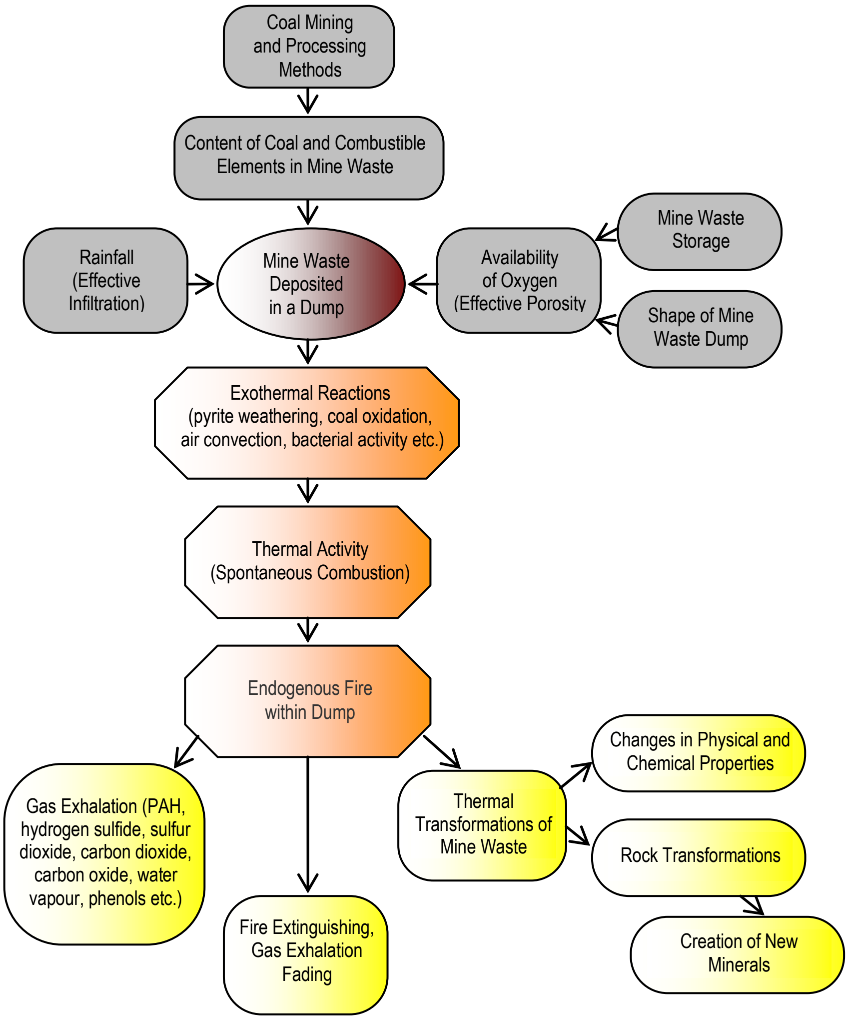

Fig. 1. Factors initiating mine waste dump fires (own studies)

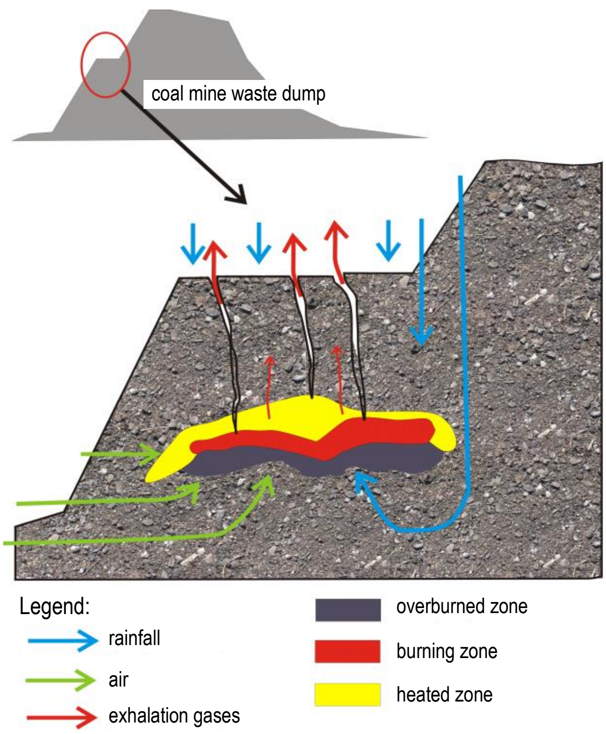

Fig. 2. Schematics of burning mine waste dump (own studies)

Photo 2. Examples of mineral forms created during thermal transformations of mine waste (Photo by P.Kuna)

3. RESEARCH OBJECT AND METHODS

3.1. Polycyclic aromatic hydrocarbons (PAH) and their creation in thermally active mine waste dumps

PAH compounds are a group of ubiquitous pollutants which are released into the natural environment mainly as a result of anthropogenic activity or due to anthropogenic factors (Nam et al. 2007). They are mainly products resulting from the incomplete combustion of organic materials, which were identified in many sources of emission e.g. exhaust fumes from cars, power plants, factories (Trapido 1999) and coking plants (Kuna 2010). Forest fires and volcanic activity is a significant natural source of PAH compounds (Smith et al. 2006). Lemieux claims (Lemieux, Lutes, Santoianni 2004) that emissions associated with the open combustion of organic matter (e.g. mine waste dump combustion, grass burning) may be actually higher than emissions from controlled sources.

The self-oxidation and self-heating of mine waste causes the intensive emission of various gases, including PAH. Coal and pyrite in the waste material undergo an oxidation process which releases heat. The increased thermal state of the ground of the dump, as well as the presence of pore water and gases containing products resulting from the slow oxidation of coal (CO, CO_2), lead to the gasification of the remaining coal substance in micro-regions of a dump, leading to the creation of hydrocarbons.

It is necessary to emphasise that the synthesis of PAH in the thermal processes of transforming solid fuels is a result of not yet fully understood multidirectional transformations which are associated with the chemical composition of the actual material. There are several models of the chemical structure of coal. What they all have in common is an assumption concerning its micromolecular and aromatic structure. In the process of degassing and primary pyrolysis, the hydroaromatic clusters and ethylene bridges present in coal generate radicals: methyl ones, ethyl ones, ethylene ones, as well as so-called precursors of polycyclic aromatic hydrocarbons (Ściążko, Zieliński 2003). Synthesis of these compounds occur cyclically through C2 and C4 radicals reacting with each other and forming C6–C4 radicals, which form the precursors of PAH. The high-energy radicals may be generated through partial cracking of aliphatic parts and/or complex organic compounds together with the synthesis of PAH precursors in the process of their fast binding (Howsam, Jones 1998).

3.2. Research methodology

PAH samples in the gas phase were collected with the use of PUF (polyurethane foam) sampling cartridges with a quartz fibre filter and an aspirator. Due to the lack of data concerning research conducted so far, and lack of methodology regarding the testing of gases emitted from mine waste dumps to determine polycyclic aromatic hydrocarbons, an attempt was taken to establish a set of rules to specify them. Samples were collected for 20 minutes; the flow of gas was 3 dm^3/min (Photo 3). The time was established on the basis of earlier experiment studies, which evaluated the concentrations of the analyses (the ones which could be determined) and the optimum time for collecting samples (Kuna, Łączny 2012). Then the adsorbed substances were extracted with hexane, using a technique called *Accelerated Solvent Extraction* (ASE). Then the extract was purified by using a technique called *Solid Phase Extraction* (*SEP*), then it was concentrated, through vaporising it in nitrogen flow, and dissolved in 1 ml of acetonitrile. All of the samples were analysed with the use of *High Performance Liquid Chromatography* (HPLC) with an FLD detector (fluorescence detection). To prepare the research methodology, the specifications of the analytical technique were prepared, which concerns collecting and determining organic compounds in the air (U.S. EPA 1999).

Photo 3. Sampling the gas (Photo by P. Kuna)

4. RESULTS OF RESEARCH

Di- and tricyclic compounds e.g. Nap, AcP, Flu, PA and Ant, were found in the analysed gas samples. Polycyclic PAH compounds e.g. fluoranthene (FLU), pyrene (PYR) or benzo[*a*]pyrene (BaP) were not observed in any of the 24 samples. This is associated with the fact that dust particles tend to increase sorption and decrease the tendency to vapourise, together with the increasing molecular mass of the given PAH compounds (Howsam, Jones 1998). The distribution of PAH compounds in gas and solid phases depends mostly on the vapour pressure of a given PAH compound and its affinity to suspended dust particles, specified with K_{oc} adsorption coefficient (Ramirez et al. 2011). That is why the determined hydrocarbons were the hydrocarbons of the highest volatility. Other PAH compounds found in the gases emitted in the burning mine waste dump were not determined. It may be associated with their lower volatility and the depositing of mineral particles in the dump.

The total amount of PAH was fully determined. It ranged between 3.659 and 25.315 mg/m^3 (on average 10.251 mg/m^3). The highest concentration, 9.911 mg/m^3, was observed for naphtalene (Nap). This helped establish that its share in the total of PAH (97%) is significant. Fluorene (Flu) and phenanthrene (PA) were also determined in larger quantities, and their average concentrations were respectively: 0.123 and 0.129 mg/m^3. The lowest concentrations were observed for acenaphthene (AcP) and anthracene (Ant), respectively 0.084 and 0.004 mg/m^3. A very high concentration of Nap in the gas phase is associated with its high volatility among all the PAH group compounds. Concentrations of Nap, Flu and PA in the gas phase could be even higher because for the applied PUF type cartridges, efficiency for di- and tricyclic compounds is approx. 35% (U.S. EPA 1999).

Establishing the content of PAH compounds in the gas phase would be necessary if the health and environmental threats to be found in thermally active sites were to be evaluated properly.

Earlier studies, by Ramirez et al. (2011), showed that the share of PAH compounds in the gas phase should be taken into account as their contribution to the total PAH is as important as the contribution of the heaviest PAH compounds, e.g. BaP. Statistical data regarding the measurement of PAH compounds in the analysed samples is presented in Table 1.

Table 1. Summary of PAH measurements of the gas phase in samples collected in Rybnik

PAH		Concentration, mg/m^3			TEFs[a]	Mw[b]	No. of rings[c]
		average	minimum	maximum			
naphthalene	Nap	9.911	3.373	24.411	0.001	128	2
acenaphthene	AcP	0.084	0.017	0.400	0.001	154	3
fluorene	Flu	0.123	0.054	0.351	0.001	166	3
phenanthrene	PA	0.129	0.054	0.314	0.001	178	3
anthracene	Ant	0.004	0.001	0.025	0.01	178	3
Total PAH	–	10.251	3.659	25.315	–	–	–

TEFs – Toxic Equivalency Factors, Mw – Molecular weight.
[a] according to (Petryl, Schmidz, Schlatter 1996);
[b, c] according to (Howsam, Jones 1998).

5. SUMMARY

Coal mine waste dumps are often thermally active sites with cracked surfaces and high internal and external temperatures. Toxic gases and flue gases are emitted through the cracks, creating exhalation zones, which are anthropogenic counterparts of volcanic solfataras. The toxic gases may include, among others, PAH group compounds.

The article presents results of research conducted in 2012. Their aim was to evaluate the content of polycyclic aromatic hydrocarbons (PAH) in these gases. Di- and tricyclic compounds, such as Nap, AcP, Flu, PA and Ant, were determined. None of the samples showed the presence of PAH compounds such as fluoranten (FluT), pyrene (PYR) or benzo(a)pyrene (BaP), and the average total of PAH compounds was 10.251 mg/m^3.

The research was undertaken because the analysed compounds showed genotoxic, mutagenie and carcinogenic properties. The current state of research regarding the discussed issue, and a common belief that the occurrence of PAH in gases emitted from burning mine waste dumps is a problem that requires detailed studies to confirm the legitimacy of the research carried out here. The conducted research showed the presence of PAH in exhalation gases, yet a detailed study of the phenomenon requires advanced comparative analyses involving several sites. The new analyses will also have to take into account the characteristics of the different sites.

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