

Distribution of chlorides and sulfates in the aeration zone of coal waste landfill and sulfides decomposition kinetics and ground-water environment acidification.

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Abstract: This article presents chemistry of deposited mining wastes of Debiensko (Upper Silesia, Poland) coal mine as well as process and dynamics of pollutants release from the wastes located on this landfill. Thee main stages of migration in the water solution have been emphasized as well as changes of chemistry and dynamics of their spreading. The article shows also the impact of pollution both in the aeration zone and upon surface and underground water in the area of landfill. It was stated that the level of water degradation caused by depositing of coal wastes is high and it is related with chlorides and sulfates and – in the last phase of rock weathering – with iron.

Key words: migration of pollutants, chlorides and sulfates, sulfide oxidation, aeration zone, mining waste, landfill

1.Introduction

The most voluminous group of wastes produced in Poland are wastes generated during search, mining, physical and chemical treatment of ores and other fossils. Wastes from power generation fossils mining constitute ca 29% [2] of overall production of wastes in Poland. Development of forecasting methods for impact of coal mining waste landfills upon underground water are very numerous but they often yield different results. In spite of the fact that each mining waste landfill features different depositing and hydro-geological as well as type of wastes, we may find some common features for all deposited wastes. For this reason, the article presents results of simulation of pollutants' transport in the aeration zone as well kinetics of distribution of iron sulfides using the mining waste landfill "Debiensko" as an instance.

2.Characteristics of the facility

The mining waste landfill of KWK „Debiensko” is located within Silesia Uplands, within the area of municipality and city Czerwionka-Leszczyny (Fig.1), in the north-eastern part of city Czerwionka, in the drainage area of Jordanek stream –

an effluent of Bierawka river joining Odra river. This landfill, with its total area of 140 ha is of upper-level character. The landfill "Debiensko" under investigation has accommodated ca 37 millions of Mg of coal wastes [1]. The age of deposited wastes is over 25 years. From the northern side this landfill is limited by Jordanek stream valley, from the east – by Furgol street and from the west by Markwioka i Przemyslow a streets and lands belonging to "Debiensko" coal mine. On the south-west and west from the landfill body, there exist an ditch discharging leakage water, named usually (Fig. 2). Further, the landfill is limited by industrial areas.

The land ordinates in the landfill area oscillate from 250,0 m a.s.l. in its north-western part to 264,0 m a.s.l. to the east. In this area there are also located sludge deposit tanks now being subject to coal recovery process.

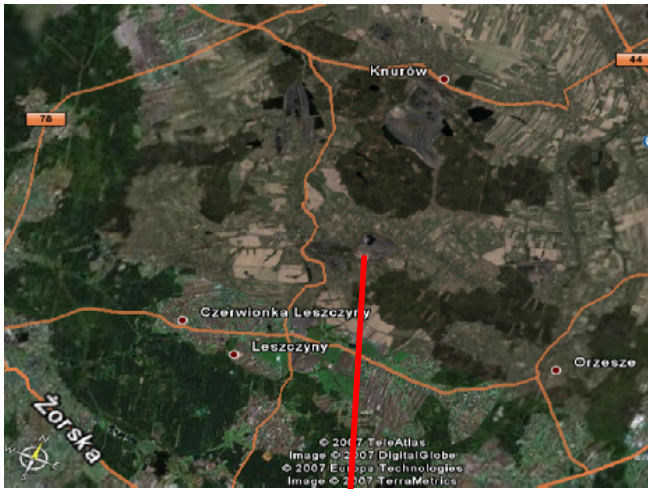


Fig.1 Overview map of coal waste landfill „Debiensko” on the background of road network and neighboring cities (Uplands Silesia, Poland)



Fig. 2 General view of coal waste landfill „Debiensko”

3. Mineralogical and physico-chemical characteristics of wastes deposited on the „Debiensko” landfill

The coal wastes deposited on the landfill „Debiensko” constitute mining and processing wastes. Mining wastes appear in the form of shale clays laminated with hard coal, claystones, mudstones, small quantities of sandstones and sporadic siderites from mudstone and Upper Silesia sandstone series. The most frequent materials in the composition of weathered rock are quartz, kaolinite and mica, and in small quantities also feldspars, siderite, chlorite, smectite, illite and pyrite. This mineral composition is supplemented by amorphous substance consisting mainly of iron hydroxides and in the case of carbonaceous shales – organic substance [1]. (tab. 1).

Table 1
Mineralogical composition of coal waste rock on the landfill (in % of volume)

Mineral composition	Rock type			
	Carbonaceous shale	Claystone	Mudstone	Sandstone
Quartz	12	22	33	62
Mica:				
- 1M _d	6	7	13	10
- 2M ₁	11	14	6	3
Kaolinite	21	23	26	15
Feldspar	4	5	4	5
Pyrite	3	2	2	1
Siderite	6	4	5	3
Chlorite + Smectite	6	5	2	<1
Amorphous substance	30	18	9	<1

Processing wastes from coal enrichment processes that are deposited on this landfill are mainly claystones and mudstones. The deposits of the lowest fraction frequently feature occurrence of organic substance in the form of pulverized coal, in quantities up to 27 % [1].

Mining wastes feature humidity from 4,8% to 7,6% and ash contents in the range from 63,4% to 83,8 %. Examples of results of water extract tests made on wastes deposited on the landfill are presented in Table 2.

Table 2
Physico-chemical analysis of water extracts from mining wastes

Parameter	Unit	Scrubber stone	Flotation wastes	Mud sludge
pH		8,8	7,8	8,0
N _{NH4}	mg/dm ³	1,62	0,66	0,42
N _{NO3}		0,55	0,33	0,22
Cl ⁻		44,0	174,0	370,0
SO ₄ ²⁻		139,0	349,0	154,0
Cd		0,001	0,001	0,001
Cr		0,01	0,01	0,01
Cu		0,01	0,02	0,01
Fe		0,10	0,10	0,10
Mn		0,01	0,02	0,01
Pb		0,03	0,01	0,03
Zn	0,01	0,01	0,01	

Water extracts from three types of coal wastes tested feature alkaline reaction in the range from 7,8 to 8,8 pH and low concentration of heavy metals. Where anions are concerned, sulfates are washed out more intensively than chlorides, which is caused by very quick leaching of chlorides during scrubbing process and in the first weeks of waste depositing. Scrubbing out of sulfates is a slower and more complex process

than chloride leaching [1]. Process and dynamics of sulfides oxidation in the landfill will be presented in the further part of this article.

Data concerning volume of sulfates and chlorides as load of pollutants washed out from carbonaceous wastes are supplemented by their lysimetric tests. The values of pollutants' loads are recalculated into concentrations in the solution filtered off the lysimeter (Table 3) [1]

Table 3

Results of lysimetric tests of coal wastes

Wastes (layer in m below land level)	Range pH	Chlorides		Sulfates	
		Load [g]	Concentra- tion [mg/l]	Load [g]	Concentra- tion [mg/l]
Fresh (0,4)	7,4-8,0	1,051	534,0	0,766	389,3
Fresh (0,8)	7,9-8,6	1,302	727,6	1,694	946,4
One year old (0,8)	7,4-8,2	1,170	599,5	2,867	1468,7
Five year old (0,8)	6,9-7,5	0,640	326,5	4,495	2293,3

Presented test results may lead to a conclusion that the leached quantities of chlorides drop already after the first hear of washing the coal wastes with water. Only half of the chloride load quantity washed out of fresh wastes is being washed out from the extracted material after five years. Whereas for washed out sulfates the observed tendency is quite reverse.

From the wastes being washed during one year, the quantity of sulfate irons is half the quantity washed out from "fresh" wastes and over two times more after five years of depositing. This phenomenon results from the process of moving sulfates generated by weathering of iron sulfides (pyrite and marcasite) contained in carbonaceous coal wastes. This phenomenon is also an effect of unbalancing the eco-chemical balance of waste depositing environment caused by the quantitative edge of sulfates generated by the weathering of sulfides over the possibilities of their neutralization mainly by the carbonate minerals (calcite, dolomite, siderite)[6]. In the cases of quantitative advantage of sulfates released from the coal wastes, the outcome is most frequently acidification of environment with all further consequences of this eco-chemical status. In the case of so called "fresh" wastes being investigated, the lysimetric filtrates have shown a slightly alkaline reaction with a acidification tendency of older filtrates (tab.3)(Fig.3). This means reduction of buffering capacities of wastes under consideration after a period of 5 years from their depositing.

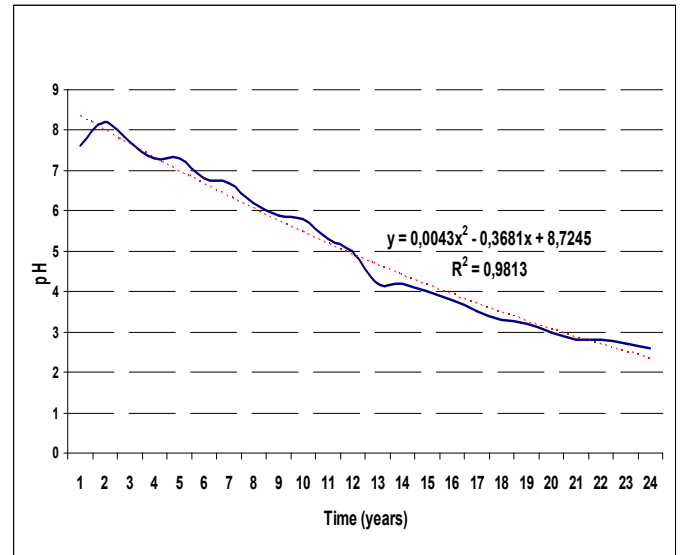
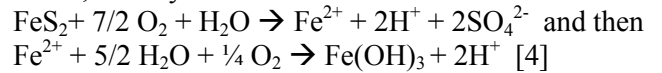


Fig. 3 Simulation of pH changeability for the filtrates from coal waste landfill over time.

4.Oxidation and decomposition of sulfides in the landfill

The sulfur contents in coal wastes originating from „Debiensko” landfill amounts in average 1,41% Sc, including ca. 1,30–1,35% Sp (sulfide or pyrite sulfur)[1]. The oxidation process of iron sulfides takes place in two stages, initially through oxidation of sulfur, then by oxidation of divalent iron:



The course and speed of these chemical reactions depend mainly from the degree of crystallization of quantities of substitutions with other metals (such as Mn, Cu or As) in the crystalline grid and from mineralogical form of the sulfides, largely depending as well of availability of oxygen and water around the mineral grains. The oxidation reaction speed for sulfites is slowed down in the presence of calcite and dolomite and – to a lesser degree – also siderite. These minerals buffer acidification of coal wastes.

An additional factor speeding up the decomposition of sulfides in the coal wastes is presence of micro-organisms, because oxidation reaction of pyrite, and especially marcasite takes place with their participation. The oxidation reaction takes place mainly in the aeration zone, where penetration of oxygen is possible. The process of sulfide leaching from coal wastes takes place in accordance with the equation of Its range kinetics with the half-leaching time oscillating within a broad range from 29 to 10 500 days with an average period of ca. 600 days. This process may be described with the following equation [4]and [5] :

$$G_s(t) = G_{s0} \cdot e^{-k \cdot t} \quad (1)$$

$$t = \frac{\ln \frac{G_s}{G_0}}{-k} \quad (2)$$

where:

$G_s(t)$ – contents of sulfide sulfur in the % of weight, remaining in the coal wastes after time t (days) from beginning of deposit (from the moment of contact with atmospheric conditions),

G_{s0} – contents of sulfide sulfur in the % of weight at the moment of bringing the rock to the surface,

k – Kinetic constant (day^{-1}),

t – time (days) counted from the beginning of depositing (from the moment of contact with atmospheric conditions),

The processes occurring within the wastes deposited on the landfill lead to significant reduction of pH of filtrates from the landfill, even below the value of 2. The product of landfill transformation is dissociated sulfuric acid that acidifies wastes and increased quantity of sulfates in the solutions. The effect of reaction lowering is higher leaching and migration of other components, such as iron, manganese, copper and arsenic. A similar situation takes place in the case of 2- and 6-valent sulfur [4] [5](Fig. 4.)

An approximate solution of sulfide decomposition course for “Debiensko” landfill we may describe in the following way: $G_s(t) = 0,01 \cdot e^{-0,0005 t}$

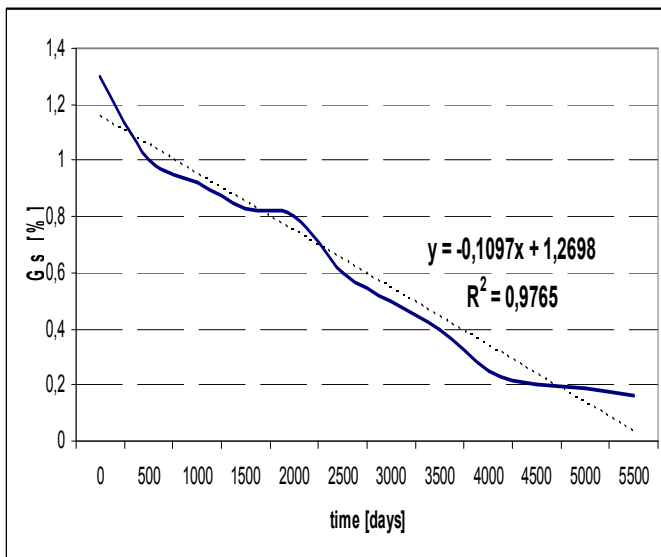


Fig. 4 Kinetics of decomposition of sulfide sulfur leaching $G_s(t)$ from coal mining wastes

5. Conclusions

1. In the first phase of water interaction on the coal wastes, chlorides are washed out and water reaction in this phase is neutral or slightly alkaline. With time, the contamination with chlorides decreases, and increases contamination due to the weathering of sulfides. The increased quantity of migrating water with high concentration of sulfates occurs in the dumps with high water permeability of landfill’s surface layer and thermally active, as a result of precipitated oxidation of pyrite in the higher temperature.

2. Increased contents of sulfates results in the reduction of buffer capacity of deposited coal wastes as well as gradual lowering of pH of pore solutions and filtrates from the landfill.

3. Low reaction is due to the presence of non-dissociated sulfuric acid generated as a result of decomposition of pyrite and marcasite that intensifies migration of metals, herein mainly iron and manganese.

4. Tests and simulations have shown a high degree of environment degradation of soil and water environment, caused by an intensive decomposition of sulfides and the multi-year character of this phenomenon causes specific problems to the environment.

5. It is necessary to reduce the oxygen access to the inside of the landfill by compaction of the deposited material thus causing reduction of water and oxygen inflow to the aeration zone of the landfill [3], which also reduces the threat of thermal activation of the facility to the minimum.

6. Creating a layer impermeable to water on the surface of deposited wastes by compacting the wastes may significantly reduce the infiltration [3] of pollutants through the aeration zone to underground water

7. The process of sulfide oxidation on the coal waste landfill „Debiensko” takes place in accordance with the it’s range kinetics equation and for the first ten years of deposition for the deposited wastes it takes the following form: $G_s(t) = 0,01 \cdot e^{-0,0005 t}$.

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