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CHEMICAL AND PHYSICAL ASPECTS OF FIRES ON COAL WASTE DUMPS

ABSTRACT

s. 131-149

Process of formation of endogenic fire is very complex mechanism that is not yet fully understood. Doubts were dispelled in the matter of main spontaneous combustion reason, which is oxidation process of coal, which is the main burning by-product material of mining operation. However, reason for activation process of self-heating and leading coal substance to critical temperature (60-80°C) is not fully understood. With that in mind, authors reviewed knowledge about experiences with spontaneous combustions of coal dumps. Learning individual stages of development of thermal anomalies on coal dump allows introduction of more effective fire prevention and fighting methods.

General characteristic of fire hazard on coal dumps has also been included. Focus has been put on causes of combustion, theories and studies on spontaneous combustion and on processes that lead to formation of endogenic fire and to stimulating its growth.

KEYWORDS

coal dump, spontaneous combustion, endogenic fire

Causes of combustion of coal waste deposited on coal dumps

To understand the essence of the processes and phenomena occurring in thermally active coal dumps, it is necessary to find out more about their genesis. Causes of combustion on coal dumps can be divided into two categories: exogenic and endogenic.

Exogenic combustion caused by interference of an outside heat sources. In most cases these fires are initiated by irresponsible behavior of people in direct contact with coal dump. Usually the causes are fire starting, incorrectly secured welding works, hot and smoldering materials. Combustion may also be initiated by random incidents such as lightning or fire migration from nearby forest. Terrestrial and underground electric cables may also prove hazardous. Preventing exogenic fires is based on regulation of human activity in the coal dump area, like banning (Fig. 1) fire starting, throwing out flammable materials and certain investments.

Endogenic combustion caused by low temperature oxidation of combustible material (mostly coal, pyrite and marcasite). This process is characterized by significant heat emission, which in consequence leads to spontaneous combustion of waste mass and formation of so called fire outbreaks.



Fig.1. Sign forbidding entrance to the area of waste rock dump belonging to KWK „Ziemowit” mine. Source: own
Rys.1. Tablica zakazująca wstępu na teren zwalowiska skały płonnej kopalni KWK „Ziemowit”. Źródło: oprac. własne

Theories and research on coal spontaneous combustion

Process of formation of endogenic fire is very complex mechanism that is not yet fully understood. Doubts were dispelled in the matter of main spontaneous combustion reason, which is oxidation process of coal, which is the main burning by-product material of mining operation. However, reason for activation process of self-heating and leading coal substance to critical temperature (60-80°C) is not yet fully understood, therefore it seems justified to utilize current knowledge about spontaneous combustion as a foundation for explaining thermal phenomena occurring on coal dumps. Research propose few possible theories on coal spontaneous combustion, including:

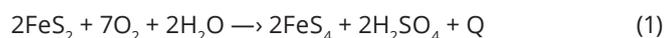
- **Bacterial theory.** Theory states that biological processes with participation of microorganisms (fermentation) have significant influence on coal spontaneous combustion process. Probable microbiological mechanism of self-heating relies on

emission of bacterial methane, which burns catalytically. Further research undermined the importance of this theory, because waste material that was sterilized, thus free of microorganisms, still had the spontaneous combustion capabilities. Bacterial theory found its use in regards to spontaneous combustion of organic substances such as hay, straw, wool, sawdust (lignin, cellulose), grain and oils [1]. Fermentation process may lead to temperature growth inside the coal dump but only in relation to wood chips deposited along with coal waste.

• **Phenol theory.** Theory based on a premise that self-heating of coal occurs due to energetic absorption of oxygen by unsaturated phenols with simultaneous heat emission.

• **Coal-oxygen complex theory.** Theory focuses on coal's ability for adsorption and chemisorption of oxygen, with simultaneous heat emission. According to this theory, ability to adsorb oxygen by coal can occur in air in normal temperature up to 0,4 cm³/g. Theory takes into account the importance of factors such as humidity and amount of fusite in coal.

• **Pyrite theory.** Pyrite (FeS₂) subjected to atmospheric oxidation, is oxidized to ferrous sulphate (H₂SO₄) and these reactions are heavily exothermic. Supporters of Pyrite theory treat coal self-heating as a process activated by catalysts dispersed within coal substance (pyrite oxidation products). Reaction presented below shows exothermic oxidation of pyrite:



Heat Q, emitted during the reaction shown above, heats up the coal substance and in proper conditions leads to spontaneous combustion of coal. Heating of coal can be initiated by pyrite when its content is higher than 5% and when it's fragmented and dispersed with high enough humidity.

The fact that coal without pyrite content also spontaneously combusts is detrimental to pyrite theory [1]. Apart from this it has to be noted that pyrite content in coal intensifies self-heating of coal, because due to oxidation it expands in volume. It results in crushing of coal and expansion of fissures, which has positive effect on oxidation.

Hypothesis suggesting that younger coal is more susceptible to combustion than the older one should also be taken into consideration. Main arguments are that younger coal has a higher content of components such as:

- Humates – amorphous, non-crystalline substances, black or brown, generated by long natural decomposition of plant matter,
- Humic acids (ground), C₆H₄O₃ – brown, amorphous, acidic substances created during natural fermentation process of plant matter,
- Oxygen.

Oxidizing humates and humic acids have capability to dynamically absorb oxygen, which causes exothermic reaction to occur that emit enough thermal energy for coal to spontaneously combust [28].

The common feature reveals itself while looking for consensus between these theories. Process of self-heating is based on oxidation of coal in oxygen environment [1]. Oxidation reactions take place even in low temperature. Specific heat of coal, which

is almost four times lower than specific heat of water, and small thermal conduction coefficient (around $0,3 \text{ W/m}^3\text{K}$ – in room temperature) causes heat, released in oxidation process, to produce relatively high thermal growth. High water content in coal delay the self-heating process due to heat loss caused by water evaporation, therefore there is an opinion that high water content – accelerates and low - delays spontaneous combustion [1].

Experimental studies conducted on hard coal are based on series of method that specify tendency of coal to spontaneously combust by specifying: amount of heat and water vapor released from separated coal sample (adiabatic calorimetry) or by measuring the ability to absorb oxygen in given external conditions. Different method of measurement of spontaneous combustion capabilities of coal is based on heating the sample in a bath, using constant temperature growth. Heat of the sample in early stage is equal to the temperature of the bath that is heating it, while in further stages it starts to exceed it as a result of exothermic processes. A measure of coal's susceptibility to spontaneous combustion is a time, after which the heat of the sample exceeds the heat of a bath.

In 1990 Cairney [2] proposed a method that allowed to specify the risk of temperature growth and smoldering of coal waste. During the research is has been observed that the mixture of coal waste with soil may not be subjected to effective burning, even though it is characterized by high (over-critical) calorific value of $9000\text{-}16000 \text{ kJ/kg}$. Suggest test of potential spontaneous combustion allows to obtain good information about the ability of coal waste to spontaneously combust in their actual deposition environment. The way in which the testing method is built gives a choice between various speeds of air flow through the sample and allows for identification of critical flow, that predispose it to combustion. During the test, a sample is formed with density equal to density on existing coal dump. Analyzed coal waste are heated simultaneously with reference sample up to $600\text{-}700^\circ\text{C}$. The line of temperature increase for first and second sample are drawn in parallel if a sample tested does not show any spontaneous combustion potential (Fig. 2a and b) [29]. Heavily inclined line of temperature increase crossed with reference sample line is a testimony for hypothetical probability of spontaneous combustion occurrence (Fig. 2b).

The higher the heat, when temperature gradient of tested sample intensifies, the higher the risk of substance of spontaneous combustion.

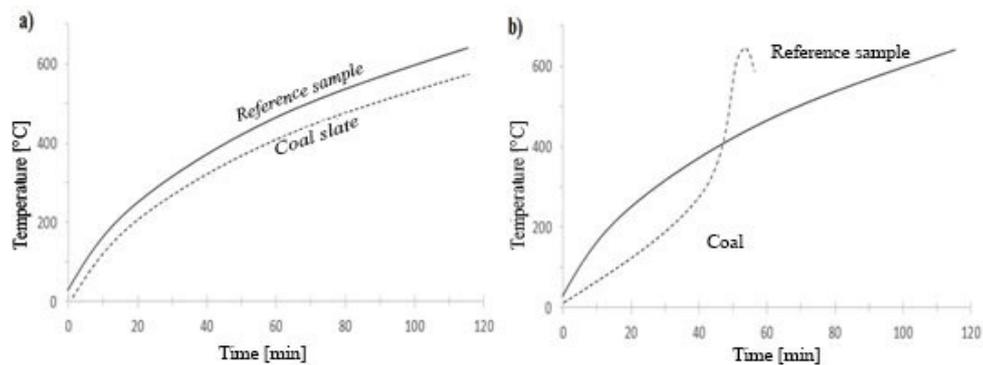


Fig. 2. Graph model of temperature increase in samples heated up to 600°C , with airflow of $2,5 \text{ L/min}$: a- test sample and coal sample [29]

Rys. 2. Modelowe wykresy przyrostu temperatury w próbach rozgrzanych do 600°C , przy przepływie powietrza $2,5 \text{ L/min}$: a) próba wzorcowa i próba łupka węglowego, b) - próba wzorcowa i próba węgla [29]

Certain problematic concept related to causes and potential of coal substance for spontaneous combustion arises after conducting studies using OTA – Oxyreactive Thermal Analysis method [3]. OTA analysis is a research method based on observation of course of reaction that a sample is subjected to during its heating [5]. It is a type of commonly used thermal differential analyses (derivatographic) [4]. Study is conducted with properly chosen factors of heating process.

To determine retrospective ambient conditions, in which initiating processes for coal dump fires occur, sample's combustion chamber uses active atmosphere change during the analysis. Additionally, it is ensured that mass of a sample is fragmented to the highest degree and spread in a fine layer on a set of plates to increase the upper limit of oxygen availability to reactive particle of studied waste. Reactions of mass increase and decrease (TG curve), emission and absorption of heat (DTA curve), their mutual causality temperature and speed, approves for legible diagnosis of studied waste substance. Apart from that measurement of differential of TG curve is registered using supporting DTG curve in minimum periods of heating time to obtain the highest degree of reaction of decrease or increase of waste substance mass [4].

OTA method is extremely accurate for specifying both the amount and quality of coal substance, registers pyrite, clay, carbonate and sulphate minerals. It is especially important considering the fact that his type of substance and mineral phases is present in particular in coal mining waste material. Simultaneity of presented substances and "following" their behavior with increase of temperature, which is often cause by spontaneous combustion of flammable material on coal dumps is fundamental direction for Oxyreactive Thermal Analysis [6, 5].

Different method testing susceptibility to spontaneous combustion of deposited material on structures formed from coal mining waste is test using a solid bed reactor to evaluate the point of combustion initiation.

This method relies on heating the samples to the starting temperature, designated by initial tests, and observing its self-increase after that. Atmosphere inside the reactor is a mixture of O₂ and N₂ chosen in such a way that it is equal to natural air composition. At the same time gaseous products such as CO, CO₂, H₂ and O₂ are measured at the reactor's outlet. Correlation of obtained measurement results allows for presentation of three-stage concept of fire development on coal waste dumps. The presented method has been used to study susceptibility to spontanous combustion of waste on „Waleska” – „Bolesław Śmiały” mine, „Wrzosey”- „Rydułtowy – Anna” mine, „Szyby Zachodnie” – „Jas-Mos” mine, coal dump at Bielszowicka street in Zabrze near old „Zabrze”mine and coal dump „Ruda” in Zabrze Biskupice.

Genesis of endogenic fires on coal dumps

Spontaneous combustion of coal waste can be generalized into multi-stage, self-accelerating burning and/or smoldering process. Content of main flammable elements in Polish mining waste deposited on coal dumps can go up to 30% of coal substance and up to 8% of pyrite and marcasite [25]. Endogenic fire hazard on structures devoted to mining waste deposition may only occur if three conditions are met simultaneously (Fig. 3) [7, 29, 12, 13].



Fig. 3. Conditions necessary for fire occurrence on coal dump. Source: own
 Rys. 3. Warunki konieczne do zaistnienia pożaru na zwalówisku powęglowym. Źródło: oprac. własne

Flammable substances deposited on coal dump along with rock material are exposed to atmosphere influence and are weathering. Simultaneously, a series of hypergenous processes start (Fig. 4) activating coal mass [1, 21]. Endogenic fire is the final result of sequence of occurrences, which precedes it.

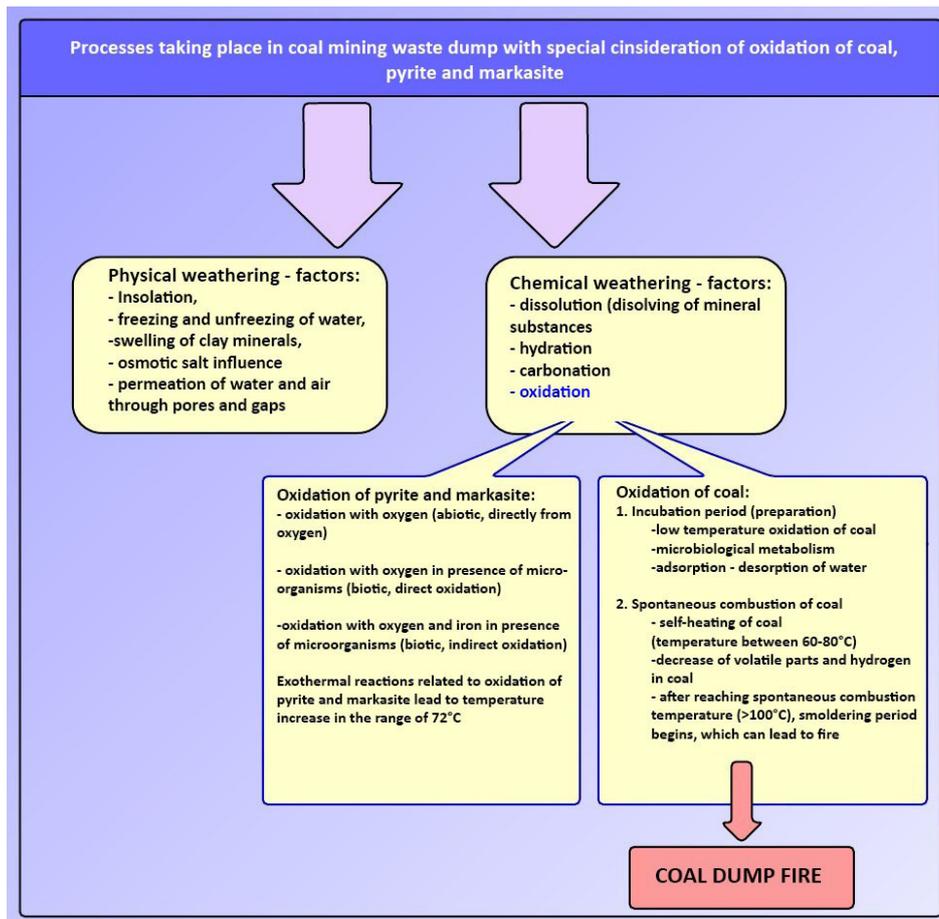


Fig. 4. Processes taking place on coal dumps. Source: own acc. to [21]
 Rys. 4. Procesy zachodzące na zwalówiskach odpadów węgla kamiennego. Źródło: oprac. własne na podst. [21]

Depending on temperature and oxygen availability, following processes of spontaneous combustion of coal can be specified (Fig. 5):

- autooxidation,
- smoldering,
- annealing,
- open flame.

The highest number of unknowns goes beyond the autooxidation process, which is described based on numerous theories, hypotheses and research. Probably, autooxidation process is molecular chain mechanism. Each particle or group of atoms in the particle, which reacted, produces active particles (one or many), which then react and catalyze neighboring particles. This process starts and lasts for a fixed amount of time in low temperature (this is so called incubation period). Such oxidation is surface process, because chemical composition of oxidized coal does not change.

Processes of smoldering and annealing are of thermal nature and can be considered in regards to thermal explosion theory.

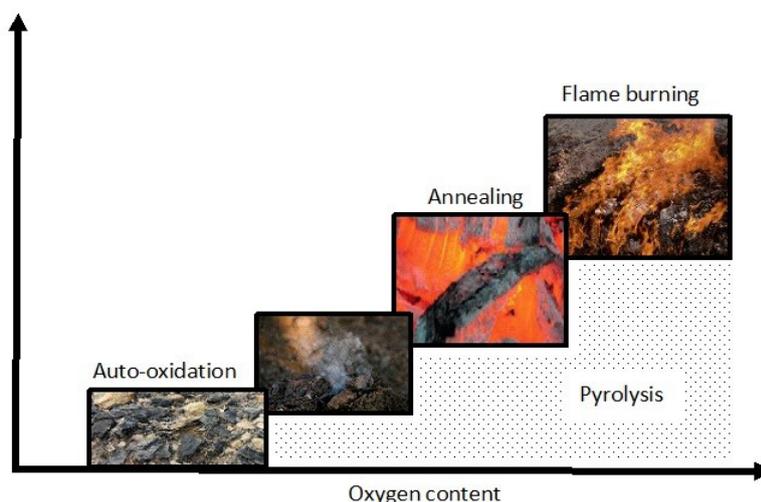


Fig. 5. Processes of reaction with air during deposition of solid fuels. Source: own acc. to [4]
 Rys. 5. Procesy reagowania z powietrzem podczas składowania paliw stałych, Źródło: oprac. własne według [4]

The experience gained over the years of research on coal waste fires allowed for designation of two periods in process of spontaneous combustion on coal dumps, corresponding to spontaneous combustion mechanism in mines and heaps (Fig. 6) [10]. The first period, known as incubation or preparatory is characterized by slow course of oxidation of organic matter and temperature similar to an ambient temperature (T_0) with minimal tendency for heat increase. Studies on coal grains surrounded by rock material shows that transport (delivery and removal of combustion products) is occurring fast enough to supply enough oxygen around coal grain (kinetics of the reaction taking place is a progress throttling factor of the process). When it comes to effectivity of heat transfer, it has been stated that its high enough to disperse the energy produced during the chemical reactions taking place. Lack of tendency for temperature increase as a result of processes occurring is specific, changes happen slowly and are dependent on temperature changes around coal grains.

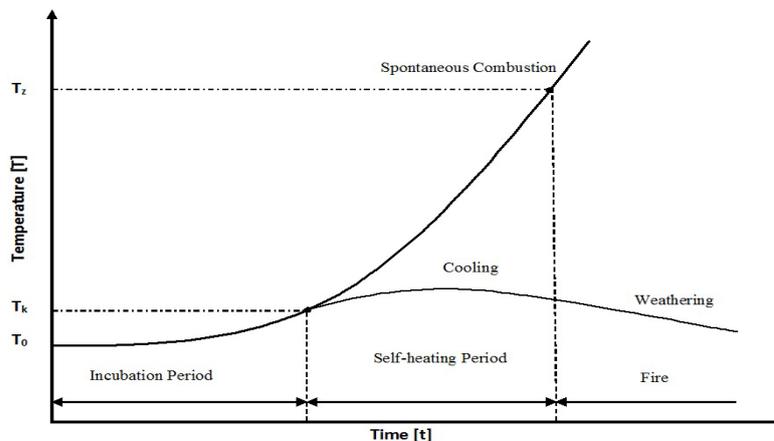


Fig. 6. Curve of coal spontaneous combustion on dump T_0 - initial temperature, T_k - critical temperature, T_z - spontaneous combustion temperature [10]
 Rys. 6. Przebieg krzywej samozapalenia węgla w składowisku T_0 - temperatura początkowa, T_k - temperatura krytyczna, T_z - temperatura samozapalenia [10]

Low temperature oxidation of coal in initial phase proceeds on the Surface of macropores in the vicinity of external surface of grains and fissures (Fig. 7) [34]. According to Adamus, the total volume of pores in coal may exceed $20 \text{ mm}^3/\text{g}$ and statistical ratio of macropores - $50 < \phi \leq 7500 \text{ nm}$ - to micropores - $50 < \phi \leq 7500 \text{ nm}$ - equals 2:3. It is observed that total free flow of molecules of gas starts from $10 \mu\text{m}$ [10000 nm). However, in situation where coal is subjected to some aerodynamic potential difference and escalation of air flow (migration), oxidation - if it persists - passes into macropores.

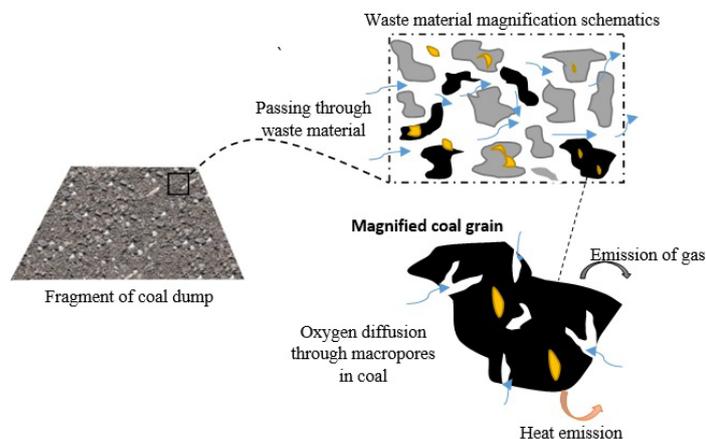


Fig. 7. Illustration showing basic phenomena occurring during low temperature oxidation of coal. Source: acc. to [34]
 Rys. 7. Ilustracja podstawowych zjawisk występujących w procesie niskotemperaturowego utleniania węgla.
 Źródło: oprac. na podst. [34]

Low temperature oxidation of coal in range up to 150°C can be described using following chemical reactions [1]:





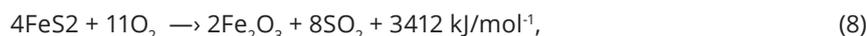
Where by oxygen adsorbed on the surface of the coal has been described by O_{oxycoal} .

Heat emitted during the reactions ($Q_I + Q_{II}$) is evaluated to be 33,4÷ 36,1 MJ/kg of coal. Thermodynamic data can be a basis for evaluation of hazard of thermal stability loss on coal dump as a result of slow oxidation of coal, based on some mathematical models [1].

During the analysis of the causes of thermal phenomena on coal dumps of Rybnik area, assumption has emerged that the coal content in waste is characterized by so called „oxyreactivity”, the tendency to form „oxycoal”, where free valence of complex coal particles, in favorable oxygen availability conditions, attract oxygen particles. This phenomenon is characterized by absence of emission of carbon monoxide and carbon dioxide. It is also assumed that in starting phase, the heating phenomenon of coal waste takes place as a result of biochemical reactions with participation of thermophilic bacteria. Twin character of biochemical occurrences taking place during composting has been suggested. Analogy can be noticed in:

- temperature increase below 60-70°C in the initial period,
- lack of CO or CO₂ emission,
- reaction progressing with oxygen access (O₂, N₂),,
- high humidity of waste material,
- heat accumulation capabilities of a structure.

During incubation coal is activated and chemical reactions with significant heat emission start. From chemical perspective spontaneous combustion of coal can be divided into three basic stages: oxidation (6), spontaneous combustion (7), burning (8÷12) [18, 11]:



Oxidation of coal accompanying pyrite and marcasite has special importance in initiation and acceleration of thermal phenomena [26]. Fromboidal pyrite is the most reactive sulfide, which can be dispersed in waste mass in form of fine grained particles with diameter of a micrometer. Oxidation of iron sulfides, coal and organic matter takes place under atmospheric oxygen and in wind aeration zone and also under the influence of oxygen dispersed in water infiltrating the dump. Oxidation of pyrite may also occur in anaerobic environment with participation of trivalent iron (Fe³⁺). It happens due to *Thiobacillus-Ferrooxidans* group of bacteria (Fig. 8).

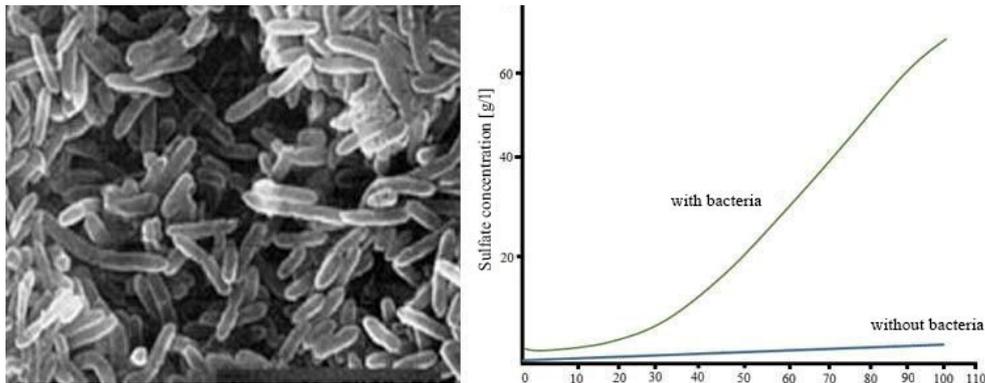


Fig. 8. On the left, view of Thiobacillus-ferrooxidans bacteria. On the right, graph showing speed of pyrite oxidation (for sulphide mining waste, temp. 21°C, pH = 3) with and without bacteria presence [35]
 Rys. 8. Z lewej widok bakterii Thiobacillus-ferrooxidans. Z prawej wykres przedstawiający szybkość utleniania pirytu (dla siarczkowych odpadów górniczych, temp. 21°C, pH = 3) w obecności lub bez bakterii [35]

Exothermic reactions related to pyrite and marcasite oxidation to ferrous sulphate and sulfuric acid lead to ambient temperature increase of 72°C. Any fine grain rock materials act as heat insulators and sustain reached temperature. Thermal energy produced is high enough that it is on the threshold of so called critical temperature (T_{cr}), which is in range of values designated for open coal dumps i.e. 60-80°C [28, 1]. At that moment the spontaneous combustion curve of coal (Fig. 6) is dependent on conditions favorable for heat dispersion and accumulation [28]. According to Saranczuk, process of self-heating up to critical temperature may take from around two months up to two years. Further oxidation of flammable substances may have three stages:

- I stage: related to situation, when temperature of organic matter does not reach critical temperature or when after reaching it there are favorable conditions for heat dispersion, then the mechanism of spontaneous combustion is interrupted and cooling process starts. Further oxygen access results in coal weathering and disappearance of properties needed for spontaneous combustion,
- II stage: flammable substance activity is at constant level,
- III stage: when accumulation of heat and exceeding of critical temperature occurs. Spontaneous combustion of organic matter enters further stage called self-heating period, when the rapid growth of temperature can be observed, which additionally impacts acceleration of oxidation processes and increased bacterial activity.

Factors influencing the rate of coal and pyrite burning

It is presumed that oxygen availability in mass of the structure, free convection and strength of the wind are factors, which control the rate of coal and pyrite oxidation on coal dump.

Free convection – described as a basic mechanism of oxygen, reagents and heat transfer (Fig. 9 and 10). Low density and favorable shape of coal dump facilitate creation of convection flow inside a mass that enables further spontaneous combustion processes [16, 17]. Observations show that self-heating process begins on steeper slopes at 3÷4 m depth from surface layer. This leads to conclusion that with improper density of slopes or when banks are not compacted at all, the favorable conditions for self-heating may appear, despite the correctly constructed structure of the remainder of the object. On the other hand, Wagner's and Králík's observations [15] prove that

endogenic fires start under surface layer of weathered material at the depth of 0,2 to 0,5 m, rarely deeper up to 5 m whereas Drenda notices that burning areas of coal dump have temperature of surface higher than ambient temperature by few degrees or in case of open fire by few hundred degrees Celsius. However deeper from surface layer the higher temperature raises dynamically to reach temperatures of 1000°C (at the depth of 8-10 m) in the hottest spot [22]. Research on thermally active objects of former USSR prove that fires, where the highest temperatures of waste material (500÷1000°C) have been registered, are located at low depths of 1,5÷2,5 from the coal dump surface. Suchariewskij observed that on flat coal dumps, areas with highest thermal activity are usually located near slopes of the coal dump, where oxygen access into the structure is relatively easy [30]. Different situation is when thermal activity on the surface of flat coal dumps, where thermal anomalies present themselves, especially near fractures and fissures in the structure. Then depths at which fires occur may be higher from 5 to 6 m.

Wind strength and direction – initiation of thermal anomalies and their highest intensity on the surface in most of the cases occurs on the scarps located windward. Strong winds fuel thermal processes. When temperature reaches 60°C and above, coal oxidation processes take lead, while in atmosphere of the coal dump CO and CO₂ appear. Very often, cases are observed where there is an intense raise of temperature and in 1-2 days' time there is a rapid increase in thermal processes in surface layers of windward slope when strong winds occur. Rybnik's „Stožki” are the prove of such phenomenon, as it has been registered, in very short time span, that temperature growth equaled from around 50-60°C up to more than 800°C. It should be pointed out that the rapid increase may occur after exceeding temperature of 130°C.

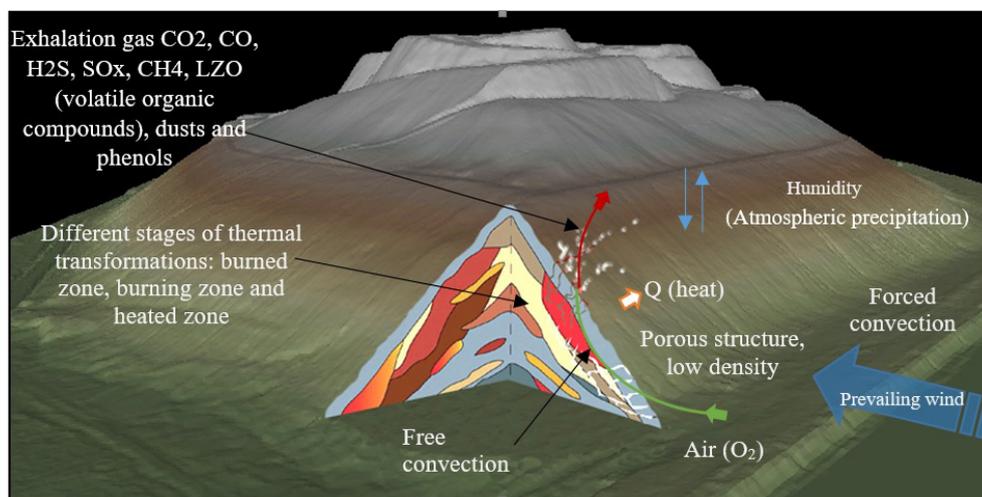


Fig. 9. Schematic of burning coal dump taking into account convection mechanisms. Source: own
 Rys. 9. Schemat zapożarowanego składowiska odpadów powęglowych z uwzględnieniem mechanizmu konwekcji. Źródło: oprac. własne

Further burning fueled by Convection steam has been shown in the Figure 10 [19]. During oxidation of coal substance attention should be brought to two parallel processes occurring:

- Activation, i.e. increase of active fire on the surface of coal dump as the evaporation proceeds and heat raises;
- Deactivation, i.e. expiration of active fires on the surface of coal dump as a result of oxygen sorption.

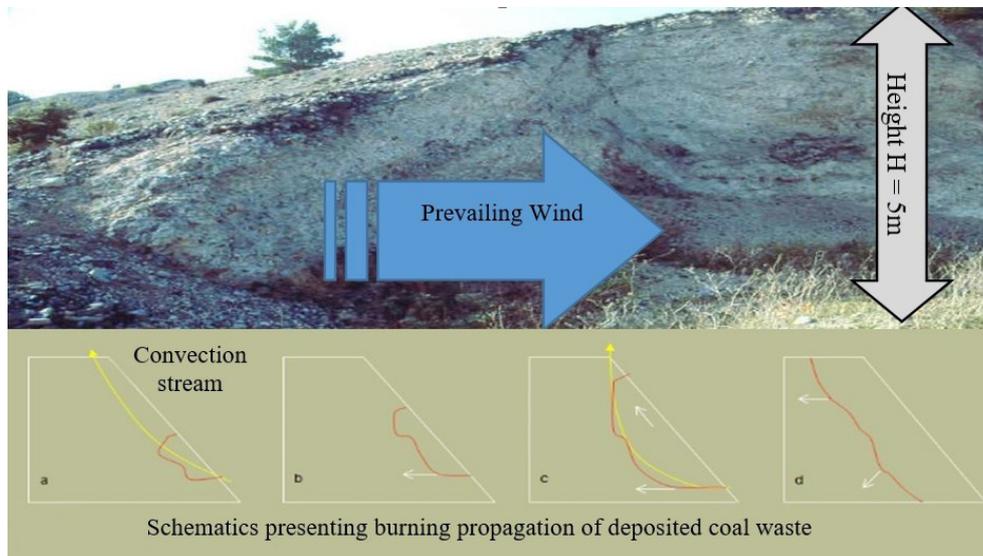


Fig. 10. Burning propagation of coal-dump waste fueled by convection stream [19]
 Rys. 10. Propagacja spalania odpadów powęglowych podsycona strumieniem konwekcyjnym [19]

Intensity of processes described above have significant influence on development of self-heating process. Increasing temperature of coal depending on its coalification reaches temperature of ignition (T_z) of around 250-350°C. On the other hand, studying ignition temperature, depending on fragmentation of coal, its value has been designated at 330-360°C for grains in size range of 1,5÷2 mm. In case of grains size of 1 mm, ignition temperatures lower to 190-220°C. Higher fragmentation facilitates access of oxygen to coal substance, increasing surface that comes in contact with oxygen, thus facilitating self-heating and spontaneous combustion process.

It is presumed that final stage of self-heating that is spontaneous combustion of coal waste is related to spontaneous combustion of vapors of sulfur, emitted during oxidation of pyrite. This phenomenon may occur in air with surface of the rock heated up by chemical reactions of pyrite leaching up to 248-261°C. Simultaneously it creates a hazard of igniting methane desorbing from sulfur.

Appearance of gasses such as CO or H₂ is a sign of reaching the fire initiation stage by the coal dump. However sometimes it happens that the high temperature inside the coal dump does not have to indicate the fire, because with simultaneous lack of CO, average (around 6-10 %) of CO₂ value and oxygen content of 10% it is considered that there is after fire state that leads to cooling of deposited material.

Urbański and Granowski [9] depending on temperature of waste material, distinct three stages of fire development:

- Self-heating of coal dump, temperature of deposited waste material in range between 40 to 150°C,
- Fire of small or average intensity, temperature of deposited waste material in range between 150 to 300°C,
- Intense fire, temperature of deposited waste material above 300°C.

Endogenic fire ends the bacterial activity; however thermal processes develop relatively fast. The decrease in sensitivity to temperature changes is characteristic, while

spontaneous combustion stops that influence. Fire spread to other areas of coal dump and further progress is reliant mainly on oxygen access and organic matter content in the waste.

The example of air and waste material temperature changes at different depths in its self-heating stage in over one-year period has been shown in the Figure 11a whereas Figure 11b illustrates distribution of isotherms on vertical cross-section of coal dump.

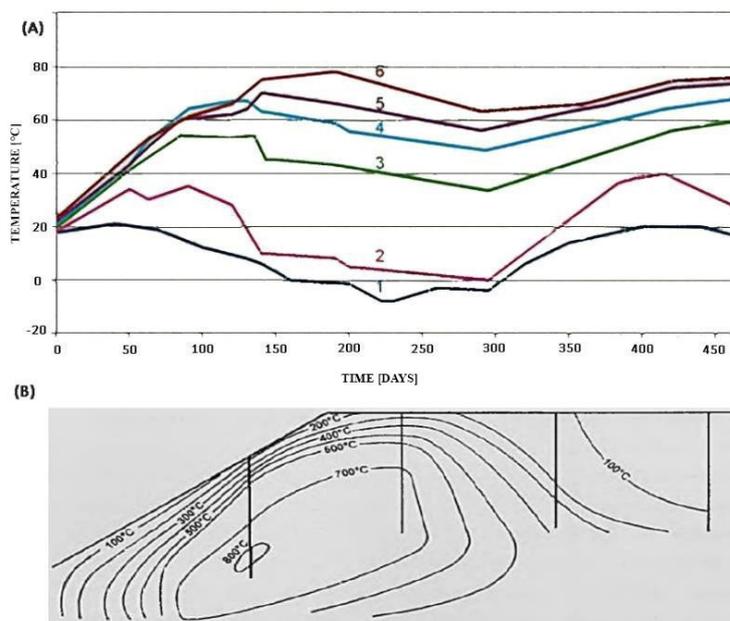


Fig.11. A) Air temperature changes (1) and waste material in it's heating phase on a surface (2), depth of 0,5 m (3), 1,0 m (4), 1,5 m (5) and 2,0 m (6) on one of dumps of the former USSR. B) Temperature distribution in zone with high thermal anomalies [26, 27]

Rys. 11. A) Zmiany temperatur powietrza (1) oraz materiału odpadowego w fazie jego zagrzewania na powierzchni (2), na głębokości 0,5 m (3), 1,0 m (4), 1,5 m (5) i 2,0 m (6) na jednej z hałd byłego ZSRR. B) Rozkład temperatur w strefie wymazującej znaczne anomalia cieplne [26, 27]

The result of limited oxygen access inside the structure is that there is a particular form of fire on coal dumps i.e. smoldering or even coking (Fig. 12). That is why burning through coal dump can take many years. Heat produced during smoldering of waste can reach up to 500°C, while oxygen concentration may from from 20% to 0,1÷ 2,5 % [22, 7, 8].

Proves of smoldering of coal waste are [31]:

- Flameless burning of waste material,
- Low peak temperature of 600 °C,
- Low burning heat of around 5 kJ/g,
- Progression of smoldering (~ 0,1 mm/s),
- Endothermic pyrolysis and exothermic oxidation,
- Deep burning in porous media,
- Burning reaction is usually incomplete,
- Presence of CH₄ and H₂O in gas measurements,
- Increased temperature in range of burning material,
- Self-sustaining of own heat,
- Burning out of organic matter and oxidation of iron compounds causes red-orange coloring of gangue (caused by thermally metamorphosed finely dispersed hematite).

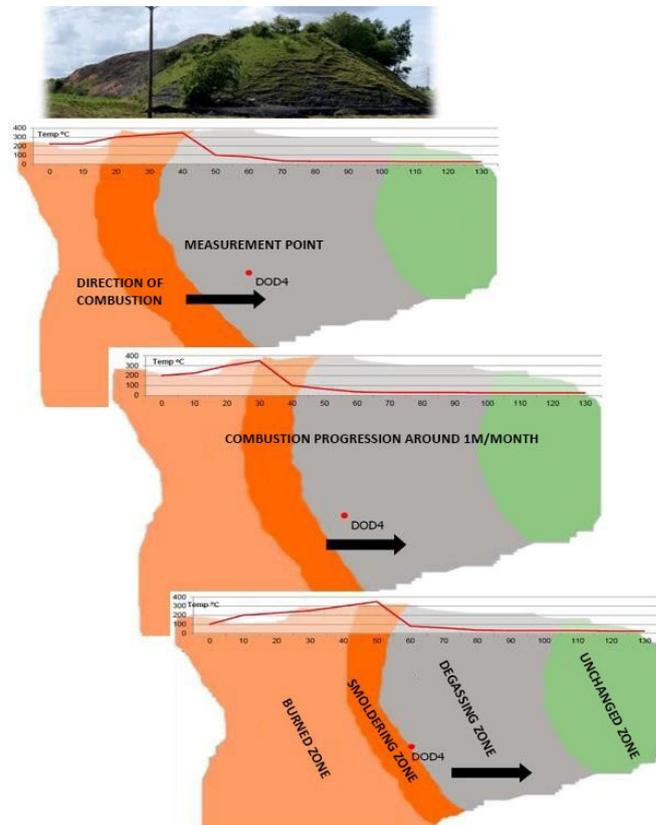


Fig.12. Burning progression in case of smoldering waste (Bogside Bing, Scotland) [33]
 Rys.12. Progresja spalania w przypadku tłuczonych odpadów (Bogside Bing Szkocja) [33]

Deposited waste contain high amount of sulfur and organic compounds, which in contact with high temperature and humidity and low oxygen access are subjected to thermal decomposition (pyrolysis) with emission of gaseous (volatile parts) and liquid products (tar). Solid coke remainder is called biochar. (Fig. 13).

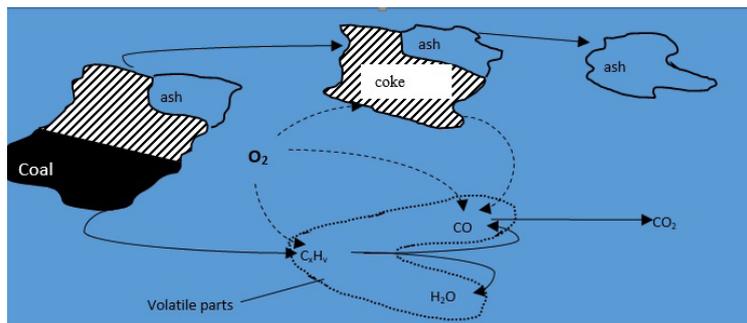


Fig. 13. Coal metamorphism during burning [1]
 Rys. 13. Przemiany węgla podczas spalania [1]

Pyrolysis of coal contained in mining waste is different from pyrolysis of industrial coal, which is conducted in controlled environment. Despite this, it is accepted to compare corresponding mechanisms in both processes.

Pyrolysis process is complex and dependent on many external factors (temperature, rate of heating and atmosphere) and type of coal. Production of tar and volatile parts is connected to coalification: in case of low coalified hard coals there are predominantly gaseous products of pyrolysis, whereas tar is prevailing in pyrolysis of highly coalified coals [1].

It appears that the pyrolysis mechanism is radical. Increase of heat causes degradation of weaker coal bonds and creation of free radicals, some of which react with hydrogen, forming volatile and liquid products, while the rest of free radicals (in polymerization, condensation and recombination processes) produce solid coke remainder [1].

Moderately coalified coals transform into plastic state, which is important for degassing mechanism (Fig. 14) [31]. Basically there are three specific stages of thermal decomposition of coal:

- I. coal - metaplast,
- II. metaplast - half-coke + tar (primary degassing in 350÷500°C),
- III. half-coke - coke + gas (secondary degassing 500°C).

In the first stage mainly water vapor is emitted and CO₂, H₂S as well as some volatile gases and tar. In second stage there is intense production of tar and gas emission increases. Third stage is characterized by decomposition of solid substance – half-coke, while the most dynamic degassing of half-coke, related to hydrogen emission takes place at temperature of 670÷720°C [32].

The amount and composition of volatile parts depends mostly on type of coal, petrography, pyrolysis conditions (pressure, temperature, atmosphere). Typical for volatile parts is high CO₂ and H₂O content. Volatile elements, with exception of carbon monoxide and hydrogen, are mainly carbohydrates. [1].

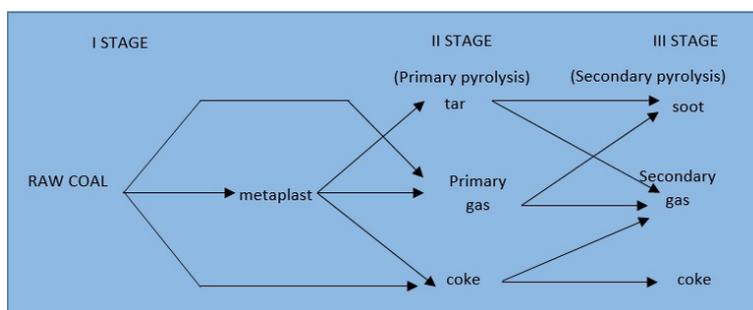


Fig. 14. Pyrolysis of coal diagram [31]
 Rys. 14. Schemat pirolizy węgla kamiennych [31]

Process of burning through coal dump proceeds very slowly and can take many years but with raise in intensity temperature can locally reach values of 1200°C [28, 23]. Accumulation of temperature inside the structure of waste dump and presence of porous water and gasses containing products of slow coal oxidation (CO, CO₂), positively influence gasification of the remainder of coal substance in micro areas of coal dump. Proper heat of coal waste causes fire of coal dump to show flame activity, when flames are visible on a surface of a structure (Fig. 15).



Fig. 15. Flame burning on coal dump Orzeł Biały – Brzeziny Śląskie (pic. Damian Cyfka)
Rys. 15. Spalanie płomieniowe na zwalowisku odpadów powęglowych Orzeł biały – Brzeziny Śląskie
(fot. Damian Cyfka)

Such high temperature interactions lead to thermal changes of organic and mineral substances. Changes mentioned depend on properties of waste material (content of: coal, hydrogen, sulfur, sodium, chloride, iron and calcium) and temperature value as well as time. Observations of burning coal dumps as well as highly variable intensity of changes in waste mass prove that temperature distribution inside the structure of coal dump is very variable [21, 24, 25, 16, 17]. It should be noted that the content of sodium, chloride, iron and calcium in waste material, supports thermal transformations of minerals, by acting like fluxes. Fluxes have properties that reduce melting temperature. That property also accelerates burning of carboniferous rocks, reducing energy required for thermal metamorphoses. Fluxes are considered to be catalysts of high temperature changes in the area of coal dump structure [16, 17]. Thermal changes taking place in coal dumps cause reduction of volume of deposited waste by 40÷60% [20], resulting in appearance of fissures that reach the surface of coal dump. Through newly formed fissures, fire gases, produced due to self-oxidation and self-heating, migrate into the atmosphere

Conclusions

Significant amount of volatile substances in rock waste from coal mines is the cause why numerous coal dumps storing this material in Upper Silesia are still endangered by thermal activity. Currently there are at least over a dozen coal dumps with thermal activity of lower and higher intensity. These coal are or may become a significant environmental problem. Considering the emission of hazardous substances into the air they are often a source of inconvenience for surrounding area. Limiting of this problem is possible using developed preventative methods and activities regarding early detection of fires. Thus it is necessary to regularly monitor the most hazardous structures. It is also important to seek more and more effective methods of prevention and fighting fires on structures built from coal waste as well as possibilities of economic utilization of this material e.g. in widely understood geoengineering.

Bibliografia

- [1] Bulewicz E., Dyjakon A., Hardy T., Kordylewski W., Słupek S., Miller R., Wanik A.: Spalanie i paliwa. Oficyna Wydawnicza Politechniki Wrocławskiej. Wrocław 2008.
- [2] Cairney T., Clucas R. C., Hobson D. 1.: Evaluating subterranean fire risks on reclaimed sites. [In:] 3rd Int. Symp. On Reclam., Treatm.. and Utiliz. Of Coal Mining Waste, Glasgow, UK, 237-242, 1990.
- [3] Cebulak S., Śmieja-Król B., Tabor A., Misz M., Jelonek I., Jelonek Z.: Oksyreaktywna Analiza Termiczna (OTA) – dobra i tania metoda oceny samozapalności węgla na składowiskach – wstępne wyniki badań. Geologia i zagadnienia ochrony środowiska w regionie górnośląskim, materiały konferencyjne LXXVI Zjazdu Naukowego Polskiego Towarzystwa Geologicznego. Rudy k/Rybnika, 14-16 września 2005.
- [4] Cebulak, S., Gardocki, M., Miczajka, M., Szlosarek, M., Tabor, A.: Wstępna ocena możliwości stosowania proszków gaśniczych w prewencji endogenicznych pożarów w obiektach zagospodarowania odpadów z wydobycia węgla kamiennego, *Górnictwo i Geologia* T. 5, z. 4, 2010.
- [5] Ciesielczuk J., Cebulak S.: Przydatność analizy termicznej do badań zmienionych termicznie odpadów powęglowych na przykładzie zwałowiska w Wojkowicach, Górnośląskie Zagłębie Węglowe, Polska. 8 czesko- polska konferencja „Geologia zagłębi węglonośnych” 2011.
- [6] Ciesielczuk J., Janeczek J., Cebulak S.: Przebieg i przyczyny endogenicznego pożaru węgla kamiennego na zrehabilitowanym składowisku odpadów komunalnych w Katowicach. *Przegląd Geologiczny*, vol. 61, nr 12, 2013.
- [7] Drenda J., Różański Z., Słota K., Wrona P.: Likwidacja zapożarowania elementem rekultywacji składowiska odpadów powęglowych w Siemianowicach Śląskich - Bańgowie. Konferencja Naukowa „Rekultywacja terenów uprzemysłowionych”. *Zeszyty Naukowe Politechniki Śląskiej* nr 1732, seria Górnictwo z. 272, s. 31-39. Gliwice 2006.
- [8] Drenda J., Różański Z., Słota K., Wrona P.: Zagrożenie pożarowe na zwałowiskach odpadów powęglowych, *Górnictwo i Geoinżynieria – Kwartalnik AGH – Polski Kongres Górniczy* 19-21.09.2007r., Uczelniane Wyd. Nauk.-Tech. AGH s.149-158, Kraków 2007.
- [9] Granowski R.: Likwidacja pożarów i zaognień hałd odpadów kopalnianych i skały płonnej oraz zapobieganie powstawaniu pożarów i zaognień. Praca specjalistyczna, 1965.
- [10] Gumiński, Różański.: Analiza aktywności termicznej śląskich składowisk odpadów powęglowych. KARBO 2005.
- [11] Jaskólkowski W., Kasperkiewicz M.: Wpływ antypirogemów stosowanych w górnictwie węgla kamiennego na ograniczenie skłonności węgla do samozapalenia. *Bezpieczeństwo i Technika Pożarnicza*, nr 3, 2012.
- [12] Korski J., Friede R., Henslok P.: Likwidacja egzogenicznych ognisk pożarowych składowiska odpadów pogórnich „Waleska” w Łaziskach Górnych. *Zeszyty naukowe Politechniki Śląskiej* Gliwice 2006.
- [13] Korski J., Henslok P., Friede R.: Uwagi o przyczynach powstania pożarów składowisk odpadów górniczych, zwalczaniu pożarów i profilaktyce przeciwpożarowej, *Seminarium IMG PAN*, Kraków 2005.
- [14] Korski J.: Termowizja w monitoringu i zwalczaniu pożarów składowisk odpadów pogórnich, *Zeszyty Naukowe Politechniki Śląskiej*, Seria Górnictwo i Geologia, t.5, z.2., 2010.
- [15] Králík J.: Tepelné změny uhlonosných sedimentů při požárech důlních odvalů a přírodním hoření uhelných slojí. Ostrava: Sborník vědeckých prací VŠB, řada hornickogeologická, roč. 30, č. 1. VŠB, s. 171–198, 1984.
- [16] Kuna P., Łączny J.M.: Zagrożenie środowiska pracy związkami WWA podczas prac rozbiórkowych składowisk odpadów powęglowych, *Biuletyn Państwowego Instytutu Geologicznego* 450: 57-62, 2012.
- [17] Kuna-Gwoździewicz P.: Wielopierścieniowe węglowodory aromatyczne w gazach stref ekshalacyjnych wybranego termicznie aktywnego składowiska odpadów wydobywczych

- z górnictwa węgla kamiennego, J. Sust. Min. Vol. 12, No 1, str. 7, 2013.
- [18] Liu C., Li S., Qiao Q., Wang J., Pan Z., Management of spontaneous combustion in coal mine waste tips in China, *Water, Air and Soil Pollution* 103, pp. 441-444, 1998.
- [19] Masalehdani N. Potdevin J.: Study of coal waste heap fires in Provence-Gardanne Coal basin, 2011.
- [20] Nichol, D., and Tovey, N.P.: Remediation and monitoring of a burning coal refuse bank affecting the Southsea Looproad at Brymbo, North Wales. *Engineering Geology* 50, pp. 309-318, 1998.
- [21] Nowak J.: Wpływ stopnia przeobrażeń termicznych odpadów powęglowych na ługowanie substancji do środowiska, *Górnictwo i Geologia*, t. 6, z. 4, Wyd. Pol. Śl., Gliwice 2011.
- [22] Patent, Polska, nr 187 753. Sposób wykorzystania ciepła z palących się hałd. Politechnika Śląska, Twórcy: J. Drenda, R. Bodora, Z. Różański., 2004.
- [23] Rainbow A.K.M.: An investigation of some factors influencing the suitability of mine stone as the fill in reinforced earth structures. *British Coal*, London 1987.
- [24] Różański H.: Skutki oddziaływania zanieczyszczeń ropopochodnych na środowisko przyrodnicze”, <http://luskiewnik.webpark.pl/luskiewnik.naftofit.html>, 2001.
- [25] Różański Z., Parchański J., Rekultywacja zwałowisk powęglowych w górnośląskim zagłębiu węglowym w aspekcie zagrożenia pożarowego, Gliwice 2009.
- [26] Różański Z.: Pozyskiwanie ciepła ze składowisk odpadów powęglowych podlegających naturalnym procesom utleniania. Praca doktorska. Politechnika Śląska, Gliwice 2003.
- [27] Saranczuk W. 1.: Borba s gorienijem parodnych otwałow. *Naukowa Dumka*, Kijow 1978.
- [28] Sawicki T.: Samozagrzewanie węgla w zwale jako przyczyna pożarów. *Karbo* 1, 2004.
- [29] Skarżyńska K.: Odpady powęglowe i ich zastosowanie w inżynierii lądowej. *Akademia rolnicza im. H. Kołłątaja*, Kraków 1997.
- [30] Suchariewskij W. M.: O pricinach i charakticrie awarii na porodnych olwalach, *Ugol*. nr 1, 1968.
- [31] Ściążko M., Zieliński H.: Termiczne przetwórstwo węgla i biomasy. Instytut Chemicznej przeróbki Węgla, Zabrze-Kraków 2003.
- [32] Tomeczek J.: Spalanie węgla, Wydawnictwo Politechniki Śląskiej, Gliwice 1992.
- [33] Torrance K., Switzer C., Keenan H., Rein G., Hadden R., Belcher, C., Carvel, R., Investigation of self-sustaining combustion of a coal waste heap in Scotland. Department of Civil Engineering, University of Strathclyde, Glasgow, UK., School of Engineering, University of Edinburgh, Edinburgh, UK.
- [34] Wang H., Długogorski B., Kennedy E.: Coal oxidation at low temperatures: oxygen consumption, oxidation products, reaction mechanism and kinetic modelling *Progres in Energy and Combustion Science*, Volume 29(6) – Jan 1, 2003.
- [35] www.codelcoeduca.cl/procesos_productivos/tecnicos_bioliixiviacion.asp

FIZYKO-CHEMICZNE ASPEKTY ZJAWISK SAMOZAPŁONÓW ZWAŁOWISK POWĘGLOWYCH

STRESZCZENIE

Proces powstawania pożarów endogenicznych jest mechanizmem bardzo złożonym i jeszcze nie do końca zrozumianym. Wątpliwości zostały „zburzone” jedynie w kwestii głównego powodu samozapłonu jakim jest proces utleniania węgla, który stanowi podstawowy materiał palny ubocznego produktu procesu wydobywczego. Niezrozumiana do końca jest przyczyna aktywacji procesu samozagrzewania oraz doprowadzenie substancji węglistej do temperatury krytycznej (60-80°C). Wobec tego w niniejszym artykule autor, dokonał przeglądu dotychczasowej podstawowej wiedzy związanej z doświadczeniami nad samoistnymi zapłonami zwałowisk powęglowych. Poznawanie poszczególnych etapów rozwoju anomalii cieplnych występujących na hałdach pozwala na wprowadzenie skuteczniejszych metod prewencyjnych, profilaktycznych, a także zwalczania ognisk pożarowych.

Przedstawiono również, ogólną charakterystykę zagrożenia pożarami na zwałowiskach odpadów powęglowych. Skupiono się na przyczynach zapłonu, teoriach i badaniach nad samozapalnością odpadów oraz na procesie powstawania pożaru endogenicznego i czynnikach stymulujących jego rozwój.

SŁOWA KLUCZOWE

zwałowisko powęglowe, pożar zwałowiska, pożar endogeniczny