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Wydanie Inżynierii Mineralnej jest dofinansowane przez dziekana Wydziału Górnictwa i Geoinżynierii Akademii Górniczo-Hutniczej.

Wspomnienie o profesorze dr. hab. inż. Wiesławie Blaschke (1941–2021)

Gdyby istniał Panteon wybitnych ludzi zasłużonych dla nauki polskiego górnictwa, Profesor miałby tam zapewne swoje miejsce. Profesor urodził się w roku 1941 w Krakowie i od najmłodszych lat już w domu rodzinnym, miał okazje obcować, z nauką górniczą. Ojciec Profesora, Pan Stanisław Blaschke był wybitnym specjalistą w dziedzinie przeróbki mechanicznej węgla, autorem podręcznika, na którym wychowywało się wielu z nas, górników.

Przed Profesorem otwierały się perspektywy, które wyznaczały kolejne etapy – w 1963 kończy Wydział Górniczy Akademii Górniczo-Hutniczej w Krakowie. W 1972 obronił pracę doktorską, a w 1983 uzyskał stopień doktora habilitowanego. Profesorem został w 2000. Zawodowy dorobek Profesora to wyniki pracy w Instytucie Przeróbki i Wykorzystywania Surowców Mineralnych AGH, Polskiej Akademii Nauk, Katedrze Przeróbki Kopalin i Utylizacji Odpadów na Wydziale Górnictwa i Geologii Politechniki Śląskiej. Tam wszędzie powstawał wielkiej wartości dorobek naukowy. Jednak szczególną wartością Jego pracy naukowej, jest użyteczność prac teoretycznych dla praktyki górniczej.



Szczególną cechą Jego działalności była ciągła współpraca z przemysłem, gdzie nie tylko konfrontował dorobek naukowy z praktyką górnictwa, ale tworzył wręcz milowe kroki w rozumieniu roli wzbogacania surowców mineralnych dla ekonomii kopalń. To jego dorobkiem są cenniki węgla handlowego oparte o uzyskane parametry węgla wzbogaconego. Szczególnie cenny, zwłaszcza w okresie wielkiej nadpodaży węgla w stosunku do wielkości wydobycia w latach 90. ubiegłego wieku, był Jego dorobek w zakresie kreowania tzw. parytetu importowego cen węgla.

Pamiętam Profesora z Jego wizyt w latach 1991-95 w KWK "Budryk", kiedy radził w sprawie modelu wówczas projektowanego i budowanego zakładu przeróbki mechanicznej węgla. Zawsze mówił do mnie, wówczas dyrektora kopalni "Budryk", że muszę wybudować kopalnię tak nowoczesną, aby jej patron Prof. Witold Budryk jej się nie wstydził - chyba to zadanie wykonaliśmy. Pamiętam też Jego częste wizyty w Ministerstwie Przemysłu i Handlu, a potem w Ministerstwie Gospodarki, gdzie dostarczał swoje opracowania, wyjątkowo cenne, dla polityki kreowania cen węgla. Wtedy też powołałem Profesora na funkcję wiceprezesa Węglozbytu S.A. - gdzie wniósł szczególny wkład w politykę obrotu węglem w kraju. Z pełnym przekonaniem powierzyłem Profesorowi funkcje w Radach Nadzorczych Spółek Węglowych, gdzie Jego kompetencje były szczególnie potrzebne.

Profesor był człowiekiem niezwykle aktywnym w stowarzyszeniach i organizacjach naukowych. Był autorem ponad 600 prac naukowych, 6 patentów, uczestnikiem wielu konferencji naukowych w całym świecie. W roku 2008 objął funkcj prezesa Stowarzyszenia Inżynierów i Techników Górnictwa, gdzie wykreował standardy trudne dla osiągnięcia przez Jego następców.

Profesor żył życiem górnictwa, uczył nas jak kojarzyć ekonomię z wydobyciem węgla, gdzie tak wiele zależy od natury. Z pełnym przekonaniem nadałem Profesorowi stopień górniczy Generalnego Dyrektora Górniczego I Stopnia. Jego dorobek dla gospodarki kraju, a zwłaszcza nauki górniczej, został doceniony przez Prezydentów RP, którzy odznaczyli Profesora Krzyżami Oficerskim i Kawalerskim Orderu Odrodzenia Polski.

Żegnając Profesora w imieniu Stowarzyszenia Inżynierów i Techników Górnictwa i całego Górniczego Stanu na krakowskim Cmentarzu Rakowickim, miałem wrażenie, tak jak wszyscy uczestnicy tej podniosłej ceremonii, że żegnam człowieka szczególnie zasłużonego i jakże potrzebnego dla górnictwa. Profesor dr hab. inż. Wiesław Blaschke był jednym z najwybitniejszych spośród nas – polskich górników.

> Szczęść Boże Profesorze, dr inż. Jerzy Markowski b. Sekretarz Stanu w Ministerstwie Przemysłu i Handlu, b. wiceminister Gospodarki, Senator RP IV i V kadencji, Prezes Stowarzyszenia Inżynierów i Techników Górnictwa

On 23.02.2021, prof. Wiesław Blaschke a scientist, university lecturer and an outstanding specialist in the field of economics of mining and hard coal processing, died at the age of 79.

During his long scientific and academic career, prof. Wiesław Blaschke was associated with the Faculty of Mining at the AGH University of Science and Technology, the Silesian University of Technology, the Institute of Mineral and Energy Economy Research Institute of the Polish Academy of Sciences, and recently with the Łukasiewicz Research Network – Institute of Mechanised Construction and Rock Mining.

Prof. Blaschke was a respected mining expert, advisor to the presidents of the State Coal Agency and the State Mining Restructuring Agency. He participated in the process of transformation of Polish hard coal mines to a free market economy.

He considered his greatest achievement to be the creation of a hard coal pricing system in 1990 that favoured improvements in coal quality.

In 1990 he became the Polish representative in the IOC/ICPC, organising with great success in Poland in 1994 – the XII International Coal Preparation Congress.

In 1995 he was the initiator and founder of the Polish Society of Mineral Processing. For a quarter of a century he was the spirit of the Society,

His motto in life was: "Life is in fact a kind of game, but to have fun you have to obey the rules of the game".

Always competent in what he did, he expressed the views to which he was convinced, he carried out every task to the best of his ability, ruthlessly sticking to the truth and nothing but the truth.

He wished everyone to fulfil their life dreams, saying that he himself had largely succeeded in doing so.

He will remain in our memories as a man of great mind and heart, universally liked and respected, and utterly devoted to his work. Dnia 23.02.2021 r. w wieku 79 lat zmarł prof. dr hab. inż. Wiesław Blaschke – naukowiec, wykładowca akademicki, wybitny specjalista w dziedzinie ekonomiki górnictwa i przeróbki węgla kamiennego.

Prof. dr hab. inż. Wiesław Blaschke w trakcie swojej wieloletniej kariery naukowej i akademickiej był związany z Wydziałem Górniczym Akademii Górniczo – Hutniczej i Politechniki Śląskiej, Instytutem Gospodarki Surowcami Mineralnymi i Energią PAN, a ostatnio z Sieć Badawcza Łukasiewicz – Instytutem Mechanizacji Budownictwa i Górnictwa Skalnego.

Prof. Blaschke był cenionym ekspertem górniczym, doradcą prezesów Państwowej Agencji Węgla Kamiennego oraz Państwowej Agencji Restrukturyzacji Górnictwa. Uczestniczył w procesie transformacji polskich kopalń węgla kamiennego do gospodarki wolnorynkowej.

Za swoje największe osiągnięcie uważał stworzenie w 1990 roku systemu cen węgla kamiennego preferującego poprawę jego jakości.

W 1990 roku został przedstawicielem Polski w IOC/ ICPC, organizując z wielkim sukcesem w Polsce w 1994 roku – XII Międzynarodowy Kongres Przeróbki Węgla.

W 1995 roku był inicjatorem i założycielem Polskiego Towarzystwa Przeróbki Surowców. Przez ćwierć wieku był duchem sprawczym Towarzystwa.

Jego dewizą życiową była myśl: "Życie jest tak naprawdę pewnym rodzajem zabawy, ale żeby zabawa ta była dobra, trzeba przestrzegać reguł gry".

Zawsze kompetentny w tym co robił, głosił poglądy, co do których był przekonany, każde zadanie wykonał najlepiej, jak tylko można, bezwzględnie trzymając się prawdy i tylko prawdy.

Każdemu życzył spełnienia jego życiowych marzeń, twierdząc, że Jemu samemu w dużym stopniu to się udało.

W naszej pamięci Pan Profesor pozostanie jako człowiek o wielkim umyśle i sercu, powszechnie lubiany i szanowany oraz bez reszty oddany swojej pracy.



Hazardous Substances and their Effects on Drinking Water Sources

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Abstract

Drinking water cannot be produced from every raw surface or groundwater in the European Union countries. The source must meet the set criteria for the raw water quaility. At present time, drinking water sources meet these requirements. However in the climate change period, accompanied in particular by long-term loss of water volumes, the set limit values for individual categories of raw water may be frequently exceeded. Human society must be prepared for this threat and take legislative and technical-operational steps in a timely manner to eliminate the risk. This paper deals with the issue in the basic scope and declares what producers and steps can be used in practice to increase the resilience of water resources to the expected change in the water quality.

Keywords: hazardous substances, drinking water sources, water quality, threat extent reduction, prevention

Introduction

Harmful, dangerous or particulary dangerous substances in water have the potential to endager human health and lives. This is not just a theoretical threat but still a real danger to statistics of individual countries or regions in the world. For example in technically and culturally advanced Europe, nearly 13.5 thousand children under the age of fourteen died in 2001 due to poor drinking water quality [1]. Outside Europe these numbers are even more threatening. With the coming climate change according to the United Nations predictions, the world 's water stress will suffer but to 3.9 miliard people [2].

It will be possible to reduce this real threat, not only by rational use of existing water resources and their expansion but also by grater emphasis on preventing surface and groundwater contamination with harmful substances. At the same time these statistics will almost certainly increase with the rapidly growing human population in Africa and a big part of Asian countries as well. Given that this predictions do not indicate a reduction in the growth rate of world's human population in the foressable future, the issue must be addressed differently. One of the possibilities is to search for new ways leading to the drinking water resources protection and their abundance in accordance with new scientific knowledge and technical possibilities of individual states in the whole world. The following chapters suggest that the solution can be implemented under the conditions of early risk awareness, its extent and means leading to its own elimination.

Water resources in the new climatic conditions of the 21st century

Water resources suitable for the treatment of raw water into drinking water are very unevenly distributed in the world. Most of them are located in relatively sparsely populated areas of the world such as Scandinavia and other water-rich areas. Altough these areas have a relative surplus of quality fresh raw water they do not meet other suitable conditions for human life, especially in terms of farming and housing constuciton with advanced public and private infrastructure, enabling a high standard of human life [3].

Due to the uneven occurence of drinking water sources on the Earth and requirements of their use for the ever increasing human population in the major regions in the world, a further increace in imbalance between requirements and natural possibilities can be expected. In addition to human population growth the current imbalance will be significantly exacerbated by climate change [4].

Its action will affect the most of natural resources that condition current human life and its needs, especially water resources. The significant decrease in water supplies at potential and real sources by up to tens percent of the original capacity can be already documented. Depending on aquatic ecosystems types and their usability for water supply purposes, climate change during the predominantly entire of the whole 21st century is likely to manifest itself in the following manner and negation extent.

Drinking water surface sources

Surface sources of drinking water will be the most important water sources in the new climatic conditions. Their importance will certainly increase with the expected reduction in groundwater volumes. However compared to groundwater, they are also more vulnerable to natural influences or anthropogenic events.

In surface water there are two main natural pollutants, two types of impuritites; dissolved high molecular weight organic substances and undissolved colloidal substances. Both pollutant groups cannot be removed from water directly by mechanical processes such as sedimentation and filtration. The particles and substances are stabilized against larger units. The main stabilization mechanisms consist of an electric double layer and a hydration cover, see figures 1 and 2.

However surface water, unlike some groundwater types, must always be treated for drinking water quality parametres. The aim of the water properties treatment is to achieve such



Fig. 1. Electronic double-layer [5] Rys. 1. Podwójna warstwa elektornowa

quality parametres of threated water as the requirements for drinking water quality in terms of its further use in the water supply processes are met. After the drinking water treatment the surface water is used as a basic medium especially for water supply systems of group and regional water mains.

Drinking water underground sources

Groundwater in general has and will continue to be irreplaceable importance for flora, fauna and also for the human population. If flora and fauna are completely existential condition for a life then in human areas they can be replaced by surface water in some built-up areas. Although in the case of scattered and other buildings they will continue to be an irreplaceable condition for people axistence in the area and technical infrastructure function of built-up areas.

Groundwater in general has diferent physical properties and composition compared to surface water. To a greater extent iron and manganese are present in dissolved form, as a simple hydrated cations Fe^{2+} and Mn^{2+} . Iron is present in groundwater in concentrations usually up to 5 mg-1. The manganese concentration is usually lower. Both substances must be removed or their content must be reduced in the process of treating raw water to drinking water. In technological processes for the iron and manganese removal from water, Fe and Mn are converted into an insoluble compound which is further separated from water by conventional methods such as sedimentation and filtration.

Insoluble compounds are prepared by oxidation of Fe and Mn to higher forms according to the reaction:

$Fe^{2+} + 3 H_2O - e = Fe(OH)_3 + 3 H^+$	(1)
$Mn^{2+} + 3 H_2O - 2e = MnO(OH)_2 + 4 H^+$	(2)

For oxidation atmospheric oxygen dissolved in water, chlorine, potassium permanganate or ozone is used as the oxidizing agent. The above mentioned substances of natural occurence in groundwater will increase during climate change and its consequences on aquatic ecocystems including the consequent need to eliminate them.

Except these substances it can be expected increased amount of following other udesirable substances in surface and groundwater:

- toxic or persistant organic compounds of various substances,
- inorganic compounds of phosphorous or elemental phosphorous,
- silage juices, industrial livestock, fertilizers,

- fluorides,
- organohalogen and organophosphorous compounds,
- mercury and its compounds,
- cyanides.

The expected increased concentrations of these above mentioned and other substances will significantly change the current natural quality of surface and groundwater to worse result. In many cases it will be neccessary to change or reconstuct existing drinking water treatment plants, given that their technology will not have the potential to treat raw, more polluted water with undesirable substances into drinking water. Due to the fact that drinking water is a completely dominant prerequisite for maintaning human health and lives, it has to meet the number of limiting and limit values. These are mainly microbiological and biological indicators, physical, chemical and organoleptic indicators and radiological indicators.

The very important part of maintaining water quality and its control is the frequency of drinking water analyzes. It will be necessary to increase drinking water quality in the water supply system compared to the current state. The primary reason will be among other things an increase in the average air and soil temperature in which water supply facilities are located as well as the expected change in the hydraulic load of drinking water mains distribution systems for public use.

Ways of eliminating threats of drinking water disposal sources by hazardous substances

Maintaining the volumetric and hydraulic yield of drinking water sources will probably be one of the most important and also very difficult tasks of the human population for at least the next decades. The result will depend mainly on two facotrs:

- climatic and meteorological conditions,
- anthropogenic threats to aquatic ecosystems.

The first factor cannot be influenced by people except in exceptional cases. However with sufficient prevention of its occurence the extent of consequences can be eliminated. The second factor and the extent of its negation in the natural environmnet including its negative impact on aquatic ecosystems, is entirely within the human capabilities and competence of the state administration, in the area of potential risk elimination and threats extent.

Climatic and meteorological conditions

Climate change and meteorological conditions cannot be significantly influenced by human population. In the pre-



Fig. 2. Hydration cover of humic substances macromolecule [5] Rys. 2. Pokrycie hydratacyjne makrocząsteczki substancji humusowych [5]

vention and alternative changes reductions some positive and negative phenomena can be used to mitigate the consequences. In water management and in aquatic ecosystems environment these are mainly the following options.

Reducing negative properties range of climatic change

- some current land deactivation of reclamation structures on agricultural land in order to prevent the outtflow of rainfall from the area (drainage systems, drainage ditches),
- surface water flow speed reduction in water recipients through newly realized water work (weirs, rafts, new meanders),
- fundamental change of management on agricultural and forest lands, especially in the form of land cultivation and secondary management in individual river basins, depending on the real environment and local climatic conditions (planting other tree species, fundamental change of agricultural crops, significant product reduction).

Natural phenomena utilization of new climatic conditions

- significant volume retention of extreme rainfall in landscape, resulting from new climatic condition manifestations (local inflitration ditches on forest and agricultural land, areas for artifical lake creation, wetlands),
- new artifical systems construction of artifical infiltration into shallow aquifers, in order to create possibility of capillary moisture in the soil environment and subsequent higher usability for agriculture (infiltration ditches, soil watering equipment, shallow wells),
- use to increase average air temperature to grow new plants and tree species and at the same time abandon the original already unsuitable crops for the newly created climatic conditions in regions (shallow rooted crops, agricultural products with high requirements for permanent soil moisture)
- usage of surface and gorund water for water supply needs for implementation to carry out anew hydrogeological survey of the area with the aim for finding weaknesses of the given area and possibility of retention strengthening and precipitationwater supply use, soil environment geological knowledge, possibility of increasing inflitration to surface water from recipients).

Both above mentioned options must be closely linked to anthropogenic potential threats arising in particular from human activity in industrial agglomerations [6]. The inter relationships of natural influences and anthropogenic events will tend to increase their negative effects when reducing the surface and groundwater volumes.

Anthropogenic threats to aquatic ecosystems

Adressing the negative effects and anthropogenic influences effects on aquatic ecosystems it is entirely within human capabilities [7]. The current scientific knowledge and technical possibilities of most countries in the world allow their solution to a sufficient extent in two basic ways.

Passive approaches to reducing the extent and anthropogenic threats consequences

- treatment processes efficiency increasing of existing wastewater treatment plants (urban and industrial wastewater treatment plants),
- current creation change of protection zones concerning water sources with the aim of significantly increasing absorption potentials in the protection zone in question (retention or harmful, dangerous organic and inorganic substances and their subsequent reduction),
- new passive elements construciton of temporary primary retention of harmful floating substances in the upper watercourses recipients (floating submerged walls, oil separators).

Active possibilities and prevention in the elimination area of anthropogenic threats to aquatic ecosystems

- elements construction and equipment limiting or completely preventing groundwater contamination (Milan walls, hydraulic barriers, monitoring wells),
- revision and significant change in the area of water management and its use in water supply and for agricultural and energy purposes (higher degree of interconnection with the crisis law, elements of critical infrastructure and ensuring emergency supply of natural elements and irreplaceable infrastructure of area with drinking water),
- setting out their responsibilities in the area of ensuring the long-term aquatic ecosystems sustainability and increasing current insufficient hydraulic parameters of water supply network and technical and operational other water works paramters.

The need to implement above mentioned model measures resulting from the threat of water scarcity to implement and maintain raw water quality in aquatic ecosystems have to become one of the human population primary tasks. Given that the task extends to a very wide range of human life and individual states infrastructure it is necessary to have a broad discussion on the topic.

Discussion

At the same time the expert and public discussion could be focused mainly on the following topics:

- current scientific knowledge evaluation on the threats posed by slimate change to different types of areas and their geological composition,
- new progressive methods development of risk analysis for water resources and water supply systems for public use,

 finding ways to apply new possibilites into practice in an economically feasible dimension and the maturity of human population individual states.

Conclusion

These presented procedures and proposed solutions aim to expand the existing discussion on already ongoing climate change and at the same time can contribute to a more comprehensive approach to risk assessment and its consequences in underestimatig the threat. The solved problem has a national and international character and it is necessary to aproach the interdisciplinary problém comprehensively [8].

Humanity no longer has much time to solve. However at the same time it has sufficient knowledge and also opportunities to eliminate the threat and its consequences properly and well-timed.

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Abstrakt

Woda pitna nie może być produkowana z każdej surowej wody powierzchniowej lub gruntowej w krajach Unii Europejskiej. Źródło musi spełniać określone kryteria jakości wody surowej. Obecnie te wymagania spełniają źródła wody pitnej. Jednak w okresie zmian klimatu, którym w szczególności towarzyszy długotrwała utrata objętości wody, ustalone wartości graniczne dla poszczególnych kategorii wód surowych mogą być często przekraczane. Społeczeństwo ludzkie musi być przygotowane na to zagrożenie i podejmować w odpowiednim czasie kroki legislacyjne i techniczno-operacyjne w celu wyeliminowania ryzyka. W niniejszym opracowaniu poruszono zagadnienie w podstawowym zakresie i deklaruje, jakie producenci i jakie kroki można zastosować w praktyce, aby zwiększyć odporność zasobów wodnych na oczekiwaną zmianę jakości wody.

Słowa kluczowe: substancje niebezpieczne, źródła wody pitnej, jakość wody, zmniejszenie zasięgu zagrożenia, zapobieganie



Zagrożenia pyłem i ich zwalczanie w zakładach przeróbki mechanicznej kopalń węgla kamiennego

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Abstrakt

W opracowaniu opisano zagadnienia związane ze zwalczaniem najistotniejszych zagrożenia pyłem węglowym, które występuje w zakładach przeróbki mechanicznej węgla kamiennego. Przedstawiono problemy występowania zagrożenia wybuchem pyłu węglowego podając źródła jego powstawania i prezentując dwuletnią statystykę występowania stref zagrożenia tym wybuchem w polskich organizacjach węglowych skupiających różne kopalnie. W opracowaniu zaprezentowano również problemy zagrożenia zdrowia pyłem węglowym w zakładach przeróbki. Podano sposób identyfikacji tego zagrożenia oraz trzyletnią statystykę stanowisk pracy zagrożonych obecnością pyłu węglowego stanowiącego zagrożenie dla zdrowia. Statystyka ta dotyczy liczby stanowisk, na których stwierdza się przekroczenie najwyższych dopuszczalnych stężeń pyłu i stanowisk, na których stężenie pyłu węglowego zawiera się w granicach 0,5 do 1 NDS. Przedstawiono również metody techniczne zwalczania zagrożeń pyłem węglowym. Opisano także rozwiązania urządzeń odpylających na mokro i sucho, będące efektem prac Instytutu Techniki Górniczej KOMAG. Podano też podstawowe akty prawne odnoszące się do zwalczania zagrożeń pyłem węglowym.

Keywords: węgiel kamienny, przeróbka mechaniczna, zagrożenie pyłem

1. Wprowadzenie

Zagrożenie pyłem występujące w zakładach górnictwa węgla kamiennego jest jednym z najistotniejszych i najbardziej niebezpiecznych. Źródłem powstawania pyłu w atmosferze stanowisk pracy są niemal wszystkie operacje technologiczne procesu pozyskiwania węgla od urabiania calizny węglowej i skał towarzyszących po załadunek wzbogaconego surowca na środki transportujące go do odbiorcy czy deponowanie na zwałach.

Powstawanie pyłu w zakładach przeróbki mechanicznej kopalni warunkowane jest szeregiem czynników, do których zaliczyć należy:

- właściwości samego węgla oraz skał towarzyszących (stopień uwęglenia, zawartość wilgoci, skład mineralny, itp.),
- sposób eksploatacji pokładu węglowego, zastosowane metody i maszyny urabiające caliznę węglową,
- sposób załadunku na środki transportu i rodzaj tych środków,
- przyjęte technologie wzbogacania surowca oraz zastosowane maszyny i urządzenia w układzie technologicznym zakładu przeróbczego.

Za maszyny i urządzenia mające najistotniejszy wpływ na generowanie pyłów zakładzie przeróbczym uznawane są wywroty, taśmowe przenośniki przebiercze, urządzenia transportujące urobek i produkty wzbogacania, kruszarki, przesiewacze klasyfikujące, podajniki wibracyjne, przesypy, zsuwnie i zsypnie.

Szacuje się, że podczas urabiania, transportu i przeróbki od 1% do 3% urobku zamienia się w pył kamienno-węglowy, z czego około 30% tego pyłu powstaje w procesach przeróbki węgla.

Pył występujący w zakładach przeróbki mechanicznej kopalń węgla kamiennego generuje dwa odmienne w swojej istocie zagrożenia. Sa nimi:

zagrożenie wybuchem,

 zagrożenie pyłem będącym czynnikiem szkodliwym dla zdrowia i uciążliwym.

Zagrożenie pyłem identyfikuje się mając za podstawę istniejące i obowiązujące akty prawne szeroko opisane w [14]. Pomiary stężenia pyłu w atmosferze wokół stanowisk pracy wykonuje się zgodnie z normą [18]. Badania zawartości pyłu i oznaczanie pyłu całkowitego na stanowiskach pracy wykonywane są metodą filtracyjno-wagową w oparciu o normę [19]. Metody pomiaru stężenia pyłu w atmosferze są doskonalone i dąży się w nich do opracowania aparatury pozwalającej na prowadzenia pomiarów ciągłych [16].

Przepisy zawarte w Rozporządzeniu Ministra Gospodarki z 28 czerwca 2002 r. [29] wymagają aby:

- oznaczenia stężenia pyłu w powietrzu, na stanowisku pracy, dokonywane były na podstawie uzyskanych wyników z serii pobranych próbek pyłu generowanego w procesie technologicznym,
- czas pobierania poszczególnych próbek pyłu był tak ustalany, aby masa pyłów osadzonych na filtrze nie przekroczyła maksymalnej wartości określonej dla danego typu przyrządu pomiarowego, a łączny czas pobierania próbek nie był krótszy, niż ustalony czas trwania zmiany roboczej i powinien obejmować co najmniej 70% czasu trwania procesu technologicznego,
- próbki pyłu, do oznaczania stężeń pyłu w powietrzu na poszczególnych stanowiskach pracy, pobierane były podczas wszystkich czynności procesu technologicznego,
- pomiary na stanowiskach pracy wykonywane były nie później niż 7 dni:
 - po oddaniu do ruchu nowego obiektu lub urządzenia,
 - przy pracach, w których może nastąpić zapylenie powietrza,

Organizacja	Liczba stref zagrożonych wybuchem pyłu 2018 rok			Liczba stref zagrożonych wybuchem pyłu 2019 rok		
	20	21	22	20	21	22
PG SA	0	0	137	0	0	133
JSW SA	1	1	38	1	1	37
Tauron Wydobycie SA	0	0	3	0	0	3
Węglokoks Kraj SA	0	0	13	0	0	6
Kopalnie samodzielne	16	16	0	16	16	0
Suma	17	17	191	17	17	179

Tab. 1. Strefy zagrożeń wybuchem pyłu węglowego w zakładach przeróbki mechanicznej kopalń węgla kamiennego [27,28]Tab. 1. Coal dust hazard zones in mechanical processing plants of hard coal mines [27,28]

- po wprowadzeniu zmian technologicznych,
- wystąpieniu zaburzeń i zmian geologicznych powodujących zmiany w stężeniu pyłu w powietrzu.

Zwrócić należy uwagę na niezwykle istotny problem, jakim jest osiadanie pyłu na elementach konstrukcji stanowiących zabudowę zakładu, maszynach oraz urządzeniach, które znajdują się w pobliżu miejsc generujących powstawanie pyłu. Pył ten wskutek podmuchów powietrza może zostać uniesiony i tym samym stworzyć realne zagrożenie powstania mieszanki wybuchowej.

Pomiar intensywności osiadania pyłu węglowego wykonywany jest na podstawie przedmiotowej normy [20].

Wobec zagrożeń pyłowych występujących w zakładzie przeróbczym węgla podejmowane są działania mające na celu ich ograniczenie lub wręcz likwidację. Są to zarówno metody techniczne jak i organizacyjne oraz administracyjno-prawne, takie jak normy, dyrektywy, rozporządzenia prowadzące do tworzenia systemów zarzadzania bezpieczeństwem [10,11,12,15,19] i instrukcji celowanych.

2. Zagrożenie wybuchem pyłu w zakładach przeróbki

Wybuch pyłu to egzotermiczna reakcji chemiczna, która przebiega w bardzo krótkim czasie. Wynikiem tej reakcji jest powstawanie znacznej ilości gazów. Pył węglowy w ilości od 50 do 1000 g/m³, zawierający powyżej 10% części lotnych, zawieszony w powietrzu stanowi mieszankę, która w wyniku inicjacji termicznej może doprowadzić do wybuchu. Należy nadmienić, że aktualnie wszystkie eksploatowane w polskich kopalniach pokłady zawierają powyżej 10% części lotnych w bezwodnej i bezpopiołowej substancji węglowej.

Intensywność występowania pyłu węglowego w zakładzie przeróbki mechanicznej kopalni jest zróżnicowana i zależy od czynności wykonywanych w poszczególnych sekcjach i stanowiskach układu technologicznego. Najwyższy poziom zapylenia identyfikowany jest w przestrzeni sekcji z procesami prowadzonymi "na sucho". Zaliczyć należy sekcje: klasyfikacji, rozdrabniania grubych sortymentów, suszenia koncentratów mułowych, sortowania i załadunku produktów handlowych. Ponadto pył generowany jest na przesypach układów transportujących urobek między sekcjami technologicznymi i zasypach zbiorników. Również możliwym miejscem powstawania zawieszonego w powietrzu pyłu węglowego są też zwały węgla.

Minimalne wymagania odnoszące się do bezpieczeństwa i higieny pracy i związane z oceną ryzyka wystąpienia atmosfery wybuchowej w miejscu pracy podane zostały Rozporządzeniu Ministra Gospodarki z dnia 8 lipca 2010 r. [31]. Ocena ta jest podstawą podziału przestrzeni, które zagrożone są wybuchem na trzy strefy. W odniesieniu do pyłu węglowego strefy te oznaczane są odpowiednio jako:

- strefa 20 jako przestrzeń w której atmosfera wybuchowa w postaci palnego pyłu w powietrzu występuje stale, często lub przez długie okresy,
- strefa 21 jako przestrzeń, w której atmosfera wybuchowa w postaci palnego pyłu w powietrzu może czasami wystąpić w trakcie normalnego działania,
- strefa 22 jako przestrzeń, w której atmosfera wybuchowa w postaci palnego pyłu w powietrzu nie występuje w trakcie działania, a w przypadku wystąpienia utrzymuje się przez krótki okres.

Prowadzone od szeregu lat okresowe analizy zagrożenia wybuchem pyłu węglowego w zakładach przeróbki mechanicznej kopalń węgla kamiennego wykazują tendencję spadkową liczby stref o tym zagrożeniu. W zdecydowanej większości zakładów przeróbczych nie występują strefy 20 i 21. Natomiast atmosfera wybuchowa w postaci palnego pyłu w powietrzu nie występuje, a w przypadku jej wystąpienia utrzymuje się przez krótki okres czasu. Jak łatwo zauważyć w ostatnich dwóch latach nastąpił nieznaczny spadek wystąpienia zagrożenia wybuchem pyłu w strefach 22.

Ilustracją tego stwierdzenia są wyniki analiz zaprezentowane w Tabeli 1 [27,28].

3. Zagrożenie pyłem jako czynnikiem szkodliwym dla zdrowia i uciążliwym

Pył węglowy powstający w procesach pozyskiwania surowca, jak wspomniano powyżej, stwarza zagrożenie wybuchem i jest także szkodliwy dla zdrowia oraz uciążliwy. Jest on drobno uziarniony i w swoim składzie zawiera wolną krzemionkę. Z uwagi na skutki zdrowotne najistotniejsze w nim są cząstki posiadające średnicę poniżej 7 μ m. Umożliwia to bowiem ich przeniknięcie do stref wymiany gazowej w płucach. Skutkiem długotrwałego przebywania w atmosferze z pyłem jest przewlekła choroba układu oddechowego – pylica płuc. Może być ona przyczyną szeregu chorób takich jak przewlekłe zapalenie oskrzeli, rozedma płuc, niewydolność układu oddechowego i układu krążenia, nadciśnienie płucne, zespół tak zwanego serca płucnego, czyli przerost mięśnia prawej komory serca, duszność, kaszel, ból w klatce piersiowej.

Rodzaj choroby jaką wywołuje pył oddziałujący na układ oddechowy zależy od rodzaju pyłu wdychalnego, a zagrożenie

Erakcia pyłu	Zawartość krzemionki w pyle, %					
Γιακόμα μγια	< 2	od 2 do 10	od 10 do 50	> 50		
Wdychalna	10	4	2	2		
Respirabilna	-	2	1	0,3		

Tab. 2. Najwyższe dopuszczalne rozporządzeniem stężenia pyłu węglowego (NDS) na stanowiskach pracy, mg/m³ [29]Tab. 2. Highest allowable concentration of coal dust (NDS) in work places, mg/m³ [29]

Tab. 3. Liczby stanowisk w zakładach przeróbczych zagrożone występowaniem pyłów [27,28] Tab. 3. Number of work places with potential coal dust hazard [27,28]

Organizacja	Liczba stanowis występowar 2018	sk zagrożonych liem pyłów rok	Liczba stanowisk zagrożonych występowaniem pyłów 2019 rok		
	> NDS	0,5-1 NDS	> NDS	0,5-1 NDS	
PG SA	143	329	125	264	
JSW SA	81	153	81	128	
Tauron Wydobycie SA	20	47	20	55	
Węglokoks Kraj SA	42	25	17	33	
Kopalnie samodzielne	29	31	22	37	
Suma	315	585	165	517	

jakie on stwarza zależy od stopnia jego stężenia. Cząstki pyłów zawierających wolną krystaliczną krzemionkę mogą wywoływać krzemicę.

Jak wynika z badań prowadzonych przez Instytut Medycyny Pracy – Państwowy Instytut Badawczy, pylica płuc jest najczęściej występującą chorobą zawodową górników. Wyniki tych badań pokazały, że w latach 2014-2018 w całym górnictwie stwierdzono łącznie 1 855 przypadków chorób zawodowych. Zachorowania na pylicę płuc kształtują się na poziomie 86,6% analizowanych chorób zawodowych. W analizowanym okresie pylicę wykryto u 1 607 górników [32].

Najwyższych dopuszczalnych stężeń szkodliwych dla zdrowia w środowisku pracy (NDS), w tym i pyłu, dotyczy Rozporządzenie Ministra Pracy i Polityki Społecznej z dnia 29 czerwca 2014 r (Dz.U. poz. 817) [29]. W rozporządzeniu tym stwierdza się, że najwyższe dopuszczalne stężenie (NDS) jest średnią stężenia ważonego, którego oddziaływanie na pracownika w ciągu dobowego 8-godzinnego i tygodniowego czasu pracy przez okres jego aktywności zawodowej. Oddziaływanie to nie powinno powodować niekorzystnych zmian w jego stanie zdrowia jak i w stanie zdrowia jego przyszłych pokoleń. Celem ustalania NDS szkodliwych dla zdrowia jest zminimalizowanie ich stężenia w środowisku pracy do poziomu, który jest akceptowalny z punktu widzenia ryzyka zdrowotnego. Rozporządzenie podaje dopuszczalne stężenia pyłu węglowego, które zależą od ilości krzemionki w nim zawartej. Wartości najwyższych dopuszczalnych stężeń pyłu podano w tabeli 2.

Niezwykle ważnymi w identyfikacji zawartości pyłu kopalnianego w atmosferze oraz jego szkodliwości są badania przeprowadzane metodami podanymi w przedmiotowych normach [21,22,23,24,25,26]. Częstotliwość wykonywania tych badań określono w Rozporządzenie Ministra Zdrowia dnia 20 kwietnia 2005 r. (Dz.U. nr 73, poz. 645 wraz ze zmianami) [30]. Pracodawca jest zobowiązany powiadomić pracowników o uzyskanych wynikach badań oraz umieszczać je na odpowiednim stanowisku pracy. Ponadto wyniki te wpisywane są w wymaganą rozporządzeniem kartę badań i archiwizowane przez okres trzech lat. W kopalniach do pobierania próbek powietrza stosowany jest powszechnie pyłomierz grawitacyjny CIP-10.

Badania zagrożenia pyłem w środowisku pracy wykonane w zakładach przeróbki mechanicznej wykazały, że prawie we wszystkich zakładach są stanowiska pracy, na których przekraczane są dopuszczalne przepisami wartości NDS [27,28]. Liczby stanowisk zagrożonych obecnością pyłów w okresie dwóch lat w poszczególnych organizacjach podane zostały w tabeli 3.

Przedstawione wyniki dwóch lat wskazują na spadek liczby stanowisk pracy w zakładach przeróbczych zagrożonych występowaniem w atmosferze pyłu węglowego. Spadek ten, w odniesieniu do najwyższego dopuszczalnego stężenia, wynosi niemal pięćdziesiąt procent.

4. Metody techniczne zwalczania zagrożeń wywołanych pyłem

Zagrożenia pyłem w zakładach przeróbczych, jak stwierdzono powyżej, zwalcza się wykorzystując metody organizacyjne i administracyjno-prawne oraz metody techniczne. Wieloletnia praktyka wykazała, że skutecznymi metodami technicznymi w zwalczaniu zagrożenia pyłem jest odpylanie lub zraszanie miejsc powstawania tego pyłu.

Odpylacze, będące urządzeniami odpylającymi na sucho lub na mokro, mają za zadanie wychwycenie pyłu węglowego powstającego w technologicznych procesach przeróbczych i transportowych.

O skuteczności rozwiązań odpylaczy świadczyć mogą wyniki przeprowadzonych badań i pomiarów w warunkach przemysłowych. Przykładem mogą być badania odpylacza przewałowego typu MB-M-25A odpylającego na mokro, które wykonane zostały w jednym z zakładów przeróbki mechanicznej kopalni węgla kamiennego, co opisano między innymi w [15]. W zakładzie tym w rejonach miejsc, w których powstaje pył węglowy, zamontowano wyciągi mające wychwycić i odprowadzić ten pył do centralnego odpylacza. Wyniki badań wskazały na kilkudziesięcio procentowe spadki ilości pyłu kopalnianego osiadającego wokół badanych stanowisk[15]. Tab. 4. Stężenia pyłu wdychalnego i respirabilnego na poszczególnych stanowiskach układu technologicznego w zakładzie przeróbki przy działającym i wyłączonym systemie zraszającym [8]

Tab. 4. Inhalable and respirable dust concentrations at individual work places of the technological system in the processing plant with the spraying
system working and switched off [8]

Stanowisko pracy	Typ frakcji pyłu	Stężenie pyłu – instalacja wyłączona, mg/m³	Stężenie pyłu – instalacja włączona, mg/m³	Skuteczność redukcji stężenia pyłu, %
1	wdychalna	11,88	5,92	50
1	respirabilna	2,02	1,20	40
2	wdychalna	5,42	2,36	57
2	respirabilna	2,06	0,52	75
з	wdychalna	3,12	1,16	63
5	respirabilna	0,57	0,21	62
1	wdychalna	5,46	1,47	73
4	respirabilna	0,91	0,12	86
5	wdychalna	3,98	1,91	52
J	respirabilna	1,35	0,67	51

Interesującym w budowie i zasadach działania są mokre urządzenia odpylające, które powstały w Instytucie Techniki Górniczej KOMAG [1,2,3,4,5,6]. Pozwalają one na stosowanie w różnych miejscach zakładu górniczego, wszędzie tam gdzie pojawia się pył. Są to urządzenia:

- typu UO, w których woda jest rozpraszana dyszami stałymi lub dyszą wirową. Skuteczności ich odpylania dochodzi do 99,7%.
- typu DCU działające na zasadzie kontaktu strugi zanieczyszczonego pyłem powietrza z kurtyną wodną.
- typu LDCU, w których połączono mokre odpylanie z labiryntowym przepływem powietrza. Urządzenie to może pracować w systemach wentylacji ssącej oraz kombinowanej.
- typu DRU, w których połączono tradycyjny natrysk wody z silną separacją odśrodkową. Ten typ urządzenia charakteryzuje się wysoką skutecznością odpylania przy stosunkowo niskich oporach przepływu.

Rozwiązaniem konstrukcyjnym o innym sposobie działania jest urządzenie odpylające na sucho z aktywnym układem tłumienia wybuchu. Zostało ono opracowane w ramach projektu rozwojowego finansowanego przez NCBR, który realizował Instytut Techniki Górniczej KOMAG wspólnie z Politechniką Warszawską [9]. Urządzenie to składa się z dwóch komór, w których znajdują się wkłady kasetowe osadzone na wspólnej ramie w metalowym koszu. Rama z wkładami kasetowymi jest połączona przesuwnie względem obudowy odpylacza. Jest ona wprawiana w ruch posuwisto zwrotny silnikiem elektrycznym i układem korbowodowym. Ruch ten powoduje stracanie pyłu, osadzającego się na tkaninie filtracyjnej, do zbiornika ulokowanego się w dole odpylacza. Podciśnienie w odpylaczu wytwarzane jest wentylatorem osiowym stanowiącym integralną część odpylacza. Odpylacz posiada aktywny system tłumienia wybuchu co pozwala na stosowanie go w przestrzeniach zagrożonych wybuchem pyłu oraz metanu.

Innym podejściem Instytutu Techniki Górniczej KOMAG w konstruowaniu urządzeń wykorzystywanych do zwalczania zagrożenia pyłowego są urządzenia zraszające wykorzystujące baterie dysz powietrzno-wodnych. Baterie te montowane są bezpośrednio w miejscach powstawania pyłu. Instalacje są zasilane wodą lub wodą ze sprężonym powietrzem, które wspomaga proces rozpylania kropel. Jednym z rozwiązań, które zastosowano w zakładach przeróbczych, jest system mgłowy PASAT. Pierwsze urządzenie zraszające tego typu wdrożone zostało w Zakładzie Przeróbki Mechanicznej Polskiej Grupy Górniczej Sp. z o.o. KWK "Bolesław Śmiały" na przesypie z kruszarki. Kolejne urządzenia tego typu zainstalowane zostały w innych miejscach tego zakładu oraz w KWK "Mysłowice-Wesoła". W kopalni tej na przesypach z przenośników stalowo-członowych na przenośniki taśmowe wdrożono także zmodyfikowany system PASAT-W.

Najnowszym rozwiązaniem zaprojektowanym przez ITG KOMAG, które ma na celu ograniczenie zagrożenia pyłem na stanowiskach pracy, jest system zraszania NEPTUN. System ten zastosowano w ZPMW Polskiej Grupy Górniczej Sp. z o.o. Oddział KWK "Bolesław Śmiały". Wykonawcą była Firma Innowacyjno-Wdrożeniowa "Elektron". Rozwiązanie to składa się z siedmiu niezależnych instalacji zraszających zabudowanych na pięciu stanowiskach [7] obsługi wskazanych przez służby kopalni. Były to:

- urządzenia załadowcze i rozładowcze zbiorników kamienia,
- urządzenia wzbogacające,
- urządzenia kruszące i transportujące,
- urządzenia załadowcze i rozładowcze zbiorników węgla,
- podajniki na poziomie +3,70 m.

W systemie zraszającym zastosowano specjalne atomizery ultradźwiękowe, które pozwalają na pracę w zakresie niskich wartości ciśnienia zarówno wody jak i sprężonego powietrza. Istotną zaletą systemu jest wytwarzanie strumienia zraszającego, który nie powoduje znaczącego zwiększenia zawilgocenia transportowanego materiału.

Po zamontowaniu systemu wykonano badania skuteczności jego działania porównując stężenia pyłu w atmosferze pięciu wymienionych stanowisk pracy przy działającym i wyłączonym systemie zraszającym [8]. Badania wykonywano przez cztery godziny dla każdego stanu pracy systemu.

Badania polegały na wyposażeniu osób pracujących na wymienionych stanowiskach zakładu w pyłomierze osobiste typu:

– CIP-10R do pomiaru frakcji respirabilnej pyłu,

– CIP-10I do pomiaru frakcji wdychalnej pyłu.

Pozyskane masy pyłu z miseczek pomiarowych zastosowanych pyłomierzy osobistych ważone były przez pracowników Laboratorium Pomiarów Zapylenia Powietrza Głównego Instytutu Górnictwa w Katowicach, które jest jednostką akredytowaną w zakresie badań w środowisku pracy przez Polskie Centrum Akredytacji. Uzyskane wyniki pozwoliły na oceną skuteczności działania zastosowanych systemów zraszania w redukcji stężenia pyłu wdychalnego i respirabilnego generowanego w procesie technologicznym. Wyniki badań przedstawione są w tabeli 4.

Wyniki przeprowadzonych badań wskazują na dużą skuteczność systemów zraszających na poszczególnych stanowiskach układu technologicznego zakładu przeróbki węgla kopalni. W wyniki działania tych systemów stężenie frakcji wdychalnej pyłu zmniejszyło się na poszczególnych stanowiskach obsługi od 50 do 73%, a frakcji respirabilnej od 40 do 85%.

5. Podsumowanie

Opisane powyżej metody i środki zwalczania zagrożenia pyłem, który występuje na stanowiskach obsługi w zakładach przeróbki mechanicznej kopalń węgla kamiennego, wskazują na istotne możliwości skutecznej walki o ograniczenie czy wręcz eliminację tego zagrożenia. Szeroka paleta rozwiązań technologicznych i konstrukcyjnych pozwala na odpowiedni ich dobór do konkretnych warunków środowiskowych i lokalizacyjnych występujących w zakładzie przeróbczym.

W opracowaniu zaprezentowane zostały osiągnięcia Instytutu Techniki Górniczej KOMAG w tym zakresie. Urządzenia, których konstrukcję opracowano w tym Instytucie znalazły zastosowanie w wielu zakładach przeróbki mechanicznej kopalń węgla kamiennego, spełniając tym samym niezwykle istotną rolę w walce o stworzenie warunków pracy najkorzystniejszych i najbezpieczniejszych dla zdrowia i życia załóg górniczych.

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Dust Hazards and their Control in Mechanical Processing Plants of Hard Coal Mines The study describes issues related to the prevention of the risk of coal dust that occurs in hard coal mechanical processing plants. Dust explosion hazards in coal processing plants were described, including their origins, and a two-year statistics on the location of dust explosion zones in the Polish coal organization associating various mines.

The study presents also health hazard related to coal dust exposure in coal preparation plants. Methods of coal dust exposure identification and a two-year statistics of workplaces with exposure to coal dust hazard are presented. The statistics are related to workplaces where the coal dust concentration limits are exceeded and workplaces where the allowable exposure limit is between 0,5 and 1. The technical methods of combating coal dust hazard are also presented.

Other dust prevention solutions such as dry and wet dust collectors developed by ITG KOMAG are described. In addition, basic regulations related to the coal dust prevention are listed.

Keywords: hard coal, mechanical processing, dust hazard



Unesco Global Geopark. Educational Priorities

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Abstract

Geopark is an area characterized by a special geological heritage, whose economic development is sustainable. This area must have a relatively uniform character, clearly defined boundaries and sufficient space to act as a stimulator of local economic development. Within the geopark, there should be a network of geological sites with significant values from the point of view of geotourism, education and science, as well as representing other, non-geological aspects (biotic, archaeological, cultural), making up the specificity of a given area as a region distinguishing in terms of nature and culture. An important aspect of the geopark's operation is a coherent strategy for the protection of geological sites, in accordance with the legal regulations in force in a given area. The idea of preserving the geological heritage for future generations and the concepts of creating Unesco Global Geopark in the Świętokrzyskie region have extensive assumptions. Indirectly, they are based on clear, historically documented relationships between man and inanimate nature, expressed in the traditions of ore and rock mining.

Keywords: park, education, protection of inanimate nature

Introduction

From the beginning of laying the foundations for environmental protection, the idea of protecting inanimate nature areas as an Earth heritage that has practical and spiritual value for present and future generations has been part of this program. A good example of the implementation of these assumptions is the creation of the world's first national park - Yellowstone in the United States, in which elements of geological heritage played a particularly important role, both from the point of view of nature protection and from the perspective of tourism development.

In later years, mainly in Western European countries, but also in Poland, a number of initiatives appeared, based on similar assumptions relating to areas with a special geological heritage. An example of these activities on a broader European scale were:

- adopting the Declaration of the Earth's memory rights in 1991,
- creation in 1993 of the European Association for the Protection of Geological Heritage ProGeo,
- UNESCO's development of the concept of geological parks (geoparks) by UNESCO in the late 1990s. The idea of creating a network of geoparks implementing a joint strategy for the protection, promotion and geotouristic use of geological heritage in the context of supporting sustainable economic development of the regions covered by them found its final in June 2000 on the Greek island of Lesvos, where the boards of four founding geoparks from France, Greece, Germany and Spain signed an official declaration on the creation of the European Geopark Network (EGN) [1]. The document prepared at the time: the "European Geopark Charter" is a set of main criteria defining the term "geopark" and guidelines for new

members (geoparks) applying to EGN. According to the records of "Charter...", the geopark is an area characterized by a special geological heritage, whose economic development is sustainable. This area must have a relatively uniform character, clearly defined boundaries and sufficient space to act as a stimulator of local economic development. Within the geopark, there should be a network of geological sites with significant values from the point of view of geotourism, education and science, as well as representing other, non-geological aspects (biotic, archaeological, cultural), making up the specificity of a given area as a region distinguishing in terms of nature and culture. An important aspect of the geopark's operation, as defined in the Charter, is a coherent strategy for the protection of geological sites, in accordance with the legal regulations in force in the given area.

Concepts of creating geological parks (geoparks) in the Świętokrzyskie region

The idea of preserving the geological heritage for future generations and the concepts of creating geological parks (geoparks) in the Świętokrzyskie region have extensive assumptions. Indirectly, they are based on clear, historically documented relations between man and inanimate nature, expressed inter alia traditions of ore and rock mining. Scientific research on these issues undertaken for many years as part of the statutory activities of the Polish Geological Institute, Polish Academy of Sciences and academic institutions indicate the key importance of protection and conservation of post-mining facilities as objects documenting the mentioned relationships, as well as having significant significance due to the aspect of deposit protection [2]. Excavations of old quarries located in the Chęciny-Kielce area, apart from scientific



Fig. 1. Kadzielnia amphitheater located in the southern part of the Kadzielnia quarry (photo: Geopark Kielce) Fig. 1. Amfiteatr Kadzielnia w południowej części kamieniołomu Kadzielnia (fot. Geopark Kielce)



Fig. 2. Wietrznia quarry in Kielce (Poland) (photo: M. Poros) Fig. 2. Kamieniołom Wietrznia w Kielcach (Polska) (fot. M. Poros)

and didactic values directly related to abiotic elements (exposing valuable geological profiles documenting characteristic rocks, fossils, minerals and geological phenomena) are also characterized by high biodiversity resulting from natural plant and animal succession this type of area. In connection with the unique landscape values, all of the above-mentioned conditions make the places associated with the former exploitation of rock raw materials and ores constitute valuable natural objects requiring appropriate legal protection and conservation measures. The high density of this type of objects in the Chęciny-Kielce area as well as their connection with other components of the natural environment required a comprehensive approach to the problem of protection and conservation of geological and mining heritage as an integral element of the natural and cultural landscape.

The concept incorporating this idea was initiated in the 1970s by the Świętokrzyski Branch of the Polish Geological Institute [3]. A practical manifestation of this activity were the activities initiated in 1991 aimed at creating the first geological park in Europe: the Chęcińsko-Kielecki Geological Landscape Park, finally established in December 1996 as the Chęcińsko-Kielecki Landscape Park [4]. The value of the newly created landscape park as an informal geopark was underlined in 2003 during an international conference under the patronage of the Polish Geological Institute in Krakow and the Center for Excellence in Abiotic Environment Research (REA) [5], devoted to the issue of conservation and legal protection of geological heritage in Central Europe.

An important problem that has been raised since the beginning of the propagation of the concept of geoparks in the Świętokrzyskie region was the administration of geological sites and large-scale forms of protection in the form of landscape parks, as well as the appropriate use of their values in geoeducation and geotourism [6, 7]. Initiatives in this area have taken place in several stages since the mid-1990s. The idea of building a Geological Education Center was sustained: in 1995 a project was created to establish such a unit, and in 2000 on the initiative of the Świętokrzyskie Department of the Polish Geological Institute in agreement with the Department of Protection The environment of the City Hall in Kielce developed its concept, [8]. Among the basic assumptions of this document were the development and promotion of the city's geotourist assets using:

- networks of geological reserves: Kadzielnia (Figure 1), Wietrznia and Ślichowice,
- the existing geological museum at the Świętokrzyskie Branch of the PGI,
- planned cubature in the Wietrznia reserve [5].

These efforts led to the establishment of a budget unit in 2003 – the Geoeducation Center, which in 2007 was renamed Geopark Kielce. Currently, the administration and geoturistic use of post-mining areas (including Kielce geological reserves located within the closed quarries Kadzielnia, Wietrznia and Ślichowice) are included in the broader strategy of establishing a UNESCO Global Geopark in the Chęciny-Kielce area operating in an international network gathering geoparks of unquestioned rank.

Protection and conservation of mining and geological heritage in the geopark area

Valuable natural areas associated with excavations of former quarries and ore mining sites located in the Chęciny-Kielce area operate in the vicinity of urbanized and indus-



Fig. 3. Documentation stand. Ślichowice (photo: Ł. Zarzycki) Fig. 3. Stanowisko dokumentacyjne. Ślichowice (fot. Ł. Zarzycki)



Fig. 4. Documentation stand. Rzepka mountain (photo: Ł. Zarzycki) Fig. 4. Stanowisko dokumentacyjne. Góra Rzepka (fot. Ł. Zarzycki)

trial areas. Therefore, the main factors affecting the Geopark area are various anthropogenic threats to the natural environment and the cultural landscape resulting from direct or indirect human pressure on valuable natural areas. Natural factors that have a negative impact in the context of the protection of geological and mining heritage are associated primarily with the succession of vegetation and mass movements within the slopes and slopes of quarries. Both of these natural factors acting in conjunction lead to lowering the scientific and didactic value of exposures, as well as their availability and geotourism attractiveness [9, 10].

The most important factors are specified in the Protection Plan of the Chęciny-Kielce Landscape Park and conservation plans or conservation tasks established for smaller forms of nature protection covering a total of almost 70% of the area covered by the geopark initiative.

The possibilities of implementing protective and maintenance measures eliminating or reducing the negative impact of the above factors depend in turn on formal, legal, administrative, technical and technological as well as budgetary conditions. The first of these include, first of all, ownership issues related to land and conditions resulting from the conservation status and existing documents specifying the possibilities and scope of conservation, maintenance or investment activities (conservation tasks or protection plans, study of conditions and spatial development and spatial development plans).

Administrative conditions primarily refer to the nature and status of the entity administering post-mining area. In the case of land managed entirely by a local government unit (commune) with ordered land ownership status, conservation and conservation measures may be financed under annual budgets and multi-annual investment programs. Such areas may additionally be covered by projects financed from external sources, including, apart from conservation activities, investment tasks related to the creation of small tourist infrastructure and/or large cubature facilities for education, tourism, science or recreation and cultural purposes [11]. An example of such scenarios in the last 20 years were closed quarries located in Kielce: Kadzielnia, Wietrznia and Ślichowice (Figure 3).

Technical and technological conditions are mainly associated with the quasi-permanent features of mining excavations remaining after mining of rock materials. These conditions most often decide on the adopted direction of reclamation and revitalization, also determining the scope and technique of maintenance operations related to cleaning the most valuable fragments of rock profiles from vegetation.

In the case of natural plant succession in post-mining areas subject to legal protection as nature reserves, undertaking conservation measures related to displaying rock profiles encounters the problem of plant cover protection (including rare and valuable taxa) resulting from the relevant provisions of the Nature Conservation Act. This problem is particularly important in protected areas related to excavations remaining after the exploitation of carbonate raw materials: Kadzielnia, Wietrznia, Ślichowice, Zelejowa, Miedzianka, Rzepka Peak (Figures 4, 5).

The morphologically diverse subsoil composed of carbonate rocks (mainly limestone and dolomite) is in many cases the site of the occurrence of valuable and protected plant species associated with the so-called xerothermic grasslands. The violation of the ecological balance of such habitats through ill-considered, incorrectly carried out conservation measures or their total abandonment is one of the main problems caus-



Fig. 5. Documentation stand. Red mountain (photo: Ł. Zarzycki) Fig. 5. Stanowisko dokumentacyjne. Czerwona Góra (fot. Ł. Zarzycki)

ing conflicts in the context of conservation and preservation of the abiotic and biotic heritage. This problem requires appropriate regulation through the development of plans for the protection of nature reserves, preceded by a detailed inventory and valorisation of biotic and abiotic elements developed by interdisciplinary scientific teams.

Inventory, valorisation and development of protection plans is the starting point for further activities related to the regulation of ownership issues, planning conservation and maintenance activities together with securing financial resources enabling their long-term, cyclical implementation. The example of the "Kadzielnia" and "Wietrznia" nature reserves shows that only permanent conservation measures, combined with investment activities making post-mining areas available as geotourism facilities, are able to bring measurable effects.

Conclusions

The effectiveness of activities related to the protection and conservation of geological and mining heritage in valuable natural areas remaining after opencast mining of rock raw materials or ores is the resultant of formal, legal, administrative, technical, technological and economic and economic conditions. The issue of managing such areas by entities capable of permanent, cyclical financing of conservation, conservation and investment activities is of key importance for the effectiveness of such activities. In addition to the aforementioned factors, a detailed, comprehensive inventory and valorisation of abiotic and biotic elements is a necessary condition, which is the basis for the development of protection plans determining the scope and direction of conservation and investment activities.

Examples of various conservation and investment activities carried out in post-mining areas under legal protection in the Chęciny-Kielce area also show that there is an urgent need to develop a model of good practices, constituting a specific set of guidelines for the entities administering the abovementioned areas. A good example in this respect is provided by the British model, presented comprehensively in the study "Geological coservation - a guide to good practice" from 2006. In Poland, model examples of the protection, conservation and development of mining and geological heritage, in addition to the Kadzielnia and Wietrznia discussed above, are primarily: Krasiejów (Science and Entertainment Park) and Jaworzno (Geosfera Jaworzno cCnter).

Author Contributions:

Michał Poros did the data collection, wrote the paper and result analysis. Wiktoria Sobczyk conceived, designed the search, wrote the paper and result analysis. Both authors have read and approved the final manuscript.

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The authors declare no conflict of interest.

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Światowy Geopark Unesco. Priorytety edukacyjne

Geopark to obszar o szczególnym dziedzictwie geologicznym, którego rozwój gospodarczy powinien być zrównoważony. Obszar ten musi mieć jednolity charakter, jasno określone granice i odpowiednią przestrzeń, aby działać jako stymulator lokalnego rozwoju gospodarczego. W obrębie geoparku powinna istnieć sieć stanowisk geologicznych o znaczących walorach z punktu widzenia geoturystyki, edukacji i nauki, a także reprezentujących inne aspekty niegeologiczne (biotyczne, archeologiczne, kulturowe), składające się na specyfikę danego obszaru jako regionu wyróżniającego się pod względem przyrodniczym i kulturowym. Ważnym aspektem działalności geoparku jest spójna strategia ochrony stanowisk geologicznych, zgodna z obowiązującymi na danym terenie przepisami prawnymi. Idea zachowania dziedzictwa geologicznego dla przyszłych pokoleń oraz koncepcja utworzenia Światowego Geoparku Unesco na terenie województwa świętokrzyskiego mają szerokie założenia. Pośrednio opierają się na klarownych, historycznie udokumentowanych związkach człowieka z przyrodą nieożywioną, wyrażonych w tradycji górnictwa rud i skał.

Słowa kluczowe: geopark, edukacja, ochrona przyrody nieożywionej



Testing the Impact of the Waste Product from Biogas Plants on Plant Germination and Initial Root Growth

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Abstract

During biogas production, anaerobic digestion of plant material rich in nutrients results in the so-called whole digestate. The application of nutrient-rich material present in digestate could have fertilising effects, especially in intensively used agricultural soils, and in crop yields that can affect the nutrient cycle. The aim of this article is to inform about possibilities of using mixture of digestate and haylage (use the fertilizing effect of both matters), and at the same time contribute to the improvement of agrochemical properties of soil. This study evaluates the effect of applying the mixture of digestate and haylage on germination and early stages of plant development. This article deals with primary test mixtures of digestate and haylage at ratios 10:1, 5:1 and 3:1 and compares the results with whole digestate applications. Simplified statistically calculated quantities showed that all examined mixtures better fertilizing effect in comparison with the control growing media. Based on the chemical analysis of the growing medias, a growing media with mixtures of digestate and haylage characterizing as growing medias with a high content of nutrients and a low amount of hazardous metal was investigated. The examined growing media thus met the limits for organic and commercial fertilizers. Fertilizing effects of growing media with mixture of digestate an laso be noted on increasing the proportion of macronutrients in the soil, reducing fertilization only throughout whole digestate.

Keywords: digestate, germination, haylage, soil, Petri dishes, biogas station, pH

Introduction

In the future, humanity will face an increase in the human population leading to more inputs needed to produce food, including arable land, while inorganic minerals and fossil fuels have been on the decline. On the other hand, biogas technology offers a competitive process to manage biodegradable waste streams and to produce renewable energy in a sustainable way. Furthermore, the nutrients present in the waste materials are preserved in the anaerobic digestate, which can be further refined into value-added products, such as organic fertilizers and soil improvers.

Anaerobic digestion is an effective method of biomass processing in biogas plants, in which the organic matter decomposes in the absence of oxygen to give two valuable products, i.e. biogas and digestate. Biogas is a very useful source of renewable energy, while digestate is considered a valuable bio-fertilizer (Yu at al., 2010; Scaliglia at al., 2017). However, Govasmark et al. (2011) and Heviánková et al. (2013) proved the possible occurrence of pathogenic bacteria and heavy metals in digestate. This is why it is important that digestate is safe if used to substitute mineral fertilizers (Vázquez-Rowe et al. 2015)

If digestate is compared with conventional organic fertilizers, i.e. livestock fertilizers, the digestate has a relatively high total nitrogen content from 0.2 to 1% by weight, higher pH (7-8), lower carbon and dry matter content ranging from 2-13%. The content of easily degradable organic substances depends on the technical solution of Biogas plant. According to Vítěz et al. (2013), however, the longer the residence time of the BPS substrate, the less readily degradable substances will be present in the resulting digestate. Many authors have agreed that digestate can be used in agricultural practice as a fertilizer. For example, according to Dimambro (2015), its introduction into agricultural practice can reduce the amount of inorganic fertilizers. According to Stoknes et al. (2016), digestate can serve as the main growing media component for the production of vegetables and mushrooms, and thus significantly improve the commercial profitability of tomatoes, cucumbers and lettuce.

Digestate is often considered as an organic fertilizer, but it contains stable organic matter, so it is rather mineral fertilizer (Heviánková et al., 2014). The use of digestate as fertilizer is limited primarily by hygiene requirements, the presence of hazardous elements and salinity. In a number of fermentation residues, higher concentrations of Cu and Zn were found, which did not comply with legislative requirements (Alburquerque et al, 2012). The export of digestate as fertilizer to agricultural land is governed by the Council Directive 91/676/EEC.

Fertilization is one of the main factors generating yield. Used properly, it helps maintain or increase soil fertility and productivity in an environmentally friendly manner. When used incorrectly, especially over a long period of time, it results in adverse changes in soil properties and other agroecosystem components, reduces plant productivity and degrades yield quality (Edmeades 2003, Gamzikov et al. 2007).

A combination of mineral fertilizer and farmyard manure enables to supply plants with nutrients for more than one vegetative growth season. Such fertilization system secures good plant nutrition with mineral nutrients for late growth and development stavage of plants (Bagdoniene, 1997).

The main weakness of digestate, however, is its pH, which is usually ranges from 8.2 to 8.6, in a wide range of digestates

AGR (%)	10:1	5:1	3:1	Digestate	Control
One dose	100	100	97,33	100	100
Double	92	94.67	96	96	97.33
doses					
Tree times	97.33	94.67	90.67	93.33	94.67
doses					
Four times	93.33	93.33	89.33	90.67	96
doses					
Five times	96	98.67	89.33	90.67	96
doses					
Six times	93	94.67	90.67	97.33	96
doses					

Tab. 1. Average germination of samples – Petri dish test Tab. 1. Średnie kiełkowanie próbek – test na szalce Petriego

Tab. 2. Scattering coefficient for average germination – Petri dish test Tab. 2. Współczynnik rozproszenia dla średniego kiełkowania – test na szalce Petriego

CVG	10:1	5:1	3:1	Digestate	Control
One dose	0	0	4.75	0	0
Double doses	7.53	2.44	4.17	7,22	2.37
Tree times doses	2.37	6.45	10.19	6.55	2.44
Four times doses	8.92	2.47	5.17	2.55	4.17
Five times doses	0	2.34	5,17	6.74	4,17
Six times doses	2.47	2.44	17.83	4.75	4.17

(Heslop and McCabe, 2012; N. Voća et al., 2005; Dimambro, 2012). The optimum pH range for most soil grown crops is between 5.5 and 7.0, being the range where plant nutrients are most available (Jensen, 2010). The pH value is most often adjusted with lime, according to a study by Jaskulska et al. (2014), however, it has been shown that this can lead to a deterioration of the agrochemical properties of the soil in the long term.

Therefore, in our study, we tried to adjust the pH using haylage, which is also organic matter and improves agrochemical conditions in agricultural land.co je cílem článku?

Materials and methods

Plant material, experimental design and growing conditions

For testing of germination we used Watercress (Lepidium sativum). Watercress is an annual herb growing to a height of 60 cm. Stems at the top of the branches, the leaves are pinnate, the leaves growing at the ground are more pronounced stalked. The flowers are arranged in clusters on the tops of the stems, are white or reddish and only about 2 mm in size. This plant was selected for testing based on the recommendations of EN 16086-2: 2012-01.

Characteristics of the growing media and nutrient solutions

We tried to bring our experiment as close as possible to real conditions, but at the same time maintain the methodology given by the EN 16086-2 standard. We used white top peat with a particle size of less than 10 mm, quartz sand in the range of 0.05-0.2 mm and kaolin Sigmaas substrate. The material would be mixed in a weight ratio of 74:20:5. After mixing, the soil was allowed to settle and then its pH was adjusted to 5.5-6.5, density 90 kg.m⁻³ \pm 20%, and EC 0.1 dS.m⁻¹. the tested digestate came from the family farm Stonava, Czech Republic. The optimal pH range for most crops grown in soil is between 5.5 and 7.0, which is the range in which plant nutrients are most available (Jensen, 2010). Digestate had ~95.67% water content, and the chemical parameters of the digestate were: TOC (39%), nitrogen (N 7.76%), phosphorus (P₂O₅ 10.5%),potassium (K₂O 30.2%), and pH 7,76. The haylage was prepared by grinding it into smaller pieces corresponding to a size of 10 mm. At the same time it contained haylage ~3223% water content, and the chemical parameters of the haylage were: TOC (41.7%), nitrogen (N 1.58%), phosphorus (P_2O_5 222%),potassium (K₂O 24,2.%), and pH 7.76.

Phytotoxicity test, microbiological analyses and agronomic traits

To assess the influence of mixtures of digestate and haylage, a phytotoxicity test was performed according to DIN EN 16086-2:2012-01, i.e. by incubating twenty seeds of Lepidium sativum (cress), a high sensitive reference species used in phytotoxicity bioassays according to Wang et al. (2001), at 20°C in Petri dishes, replicated tree times.

We prepared growing media in Petri dishes by adding digestate and haylage under conditions of 10:1 (3.15 g of digestate and 0.35 g of haylage), 5:1 (2.92 g of digestate and 0.58 g of haylage) and 3:1 (2.62 g digestate and 0.88 g of haylage) and whole digestate (3.5 g of digestate), three Petri dishes were used as controls. The sealed foil-sealed Petri dishes are incubated for 72 hours at an angle of 70° to 80° to the horizontal, with the seeds sown at the top and the growing media at the bottom, in the dark at a constant value of 25 ± 5 °C.

Seventy two hours after germination, the germination index percentage (GI%) was calculated according to the formula $GI\% = 100 \times (G1/G2) \times (R1/R2)$, where G1 and G2 are germinated seeds in the sample and control, and R1 and R2 are mean root lengths for the sample and for the control, respectively.

The concentration of mixures matters (digestate and haylage) was then increased by adding a given proportion of digestate and hay again to the same Petri dishes, and new watercress seeds were reseeded after 4 hours. The fifth replicates of these increasing concentration were performed in this way.

Flame AAS analysis and GC analysis

These analyses were performed on flame atomic absorption spectrometry (AAS) using Mehlich-3 extraction (Mehlich,

RI (%)	10:1	5:1	3:1	Digestate	Control
One dose	104.27	119.03	110.30	111.97	100
Double	118.23	125.48	120.92	128.76	100
doses					
Tree times	142.17	126.37	120.29	126.74	100
doses					
Four times	139.18	129.54	117.53	133.66	100
doses					
Five times	137.63	159.94	128.35	131.49	100
doses					
Six times	144.15	134.04	131.26	131.45	100
doses					

Tab. 3. Root length index – Petri dish test Tab. 3. Wskaźnik długości korzenia – test na szalce Petriego

Tab. 4. Munoo-Liis vitality index – Petri dish test Tab. 4. Wskaźnik witalności Munoo-Liisa – test na szalce Petriego

MLV (%)	10:1	5:1	3:1	Digestate	Control
One dose	104.27	119.03	107.32	111.97	100
Double	112.03	122.03	119.62	127.53	100
doses					
Tree times	146.16	126.68	115.30	124.97	100
doses					
Four times	136.29	126.13	109.77	126.36	100
doses					
Five times	137.63	164.51	119.98	124.66	100
doses					
Six times	140.37	132.30	128.14	133.07	100
doses					

1984; Wolf and Beegle, 1994). The suitability of the extraction solution Mehlich 3 for determination of fertiliser requirement was tested using the correlations between the contents of the corresponding plant nutrients in the parallel soil-plant samples. According to Sen Tran & Simards (1993), the extraction solution according to the Mehlich 3 method consists of : 0.2 N CH- $_3$ COOH, 0.25 N NH₄NO₃, 0.013 N HNO₃, 0.015 N NH₄F and 0.001 M EDTA – combines microelements into complex compounds and avoids precipitation of Ca. Phosphorus, potassium, magnesium, copper and manganese were determined from the plant material by dry ashing of office analytical method: K – 71/250 EEC; Mg, Mn – 78/633 EEC.

For determination of nutrients in soil (phosphorus, ammonia nitrogen - N-NH⁴⁺, nitrite nitrogen - NO³) by GC analysis was carried out with a gas chromatograph equipped with a flame photometric detector (P-filter) with using Mehlich-3 extraction (Mehlich, 1984; Wolf and Beegle, 1994). Macronutrients in soil (Ca, Mg, K, Na) were determined using Gilligam solution (Gillman, 1976).

All chemical analyses were made at a Czech accredited laboratory.

Statistical analysis

Experimental data were analysed using software Statistica for factorial analysis of variance (ANOVA). Multivariate data analysis was performed using principal component analysis (PCA) to assess the existing relationships between the variables examined and the parameters recorded.

Results and discussion

Today, soilless cultivation systems use large amounts of non-renewable materials (Ronga et al., 2016); Therefore, alternative growing medias are needed to improve the sustainability of production. Digestate (mainly solid digestate) appears to be suitable as a growing media (Stoknes et al., 2016), although, as some reports on compost suggest, high pH promotes their mixing with other matrices capable of reducing this value (Bugbee, 1996; Ronga et al., 2016). The results of the measured root lengths and the calculated percentage of germination from the number of germinated seeds, from tests on Petri dishes, were further used in the calculations of statistical quantities determined by the standard EN 16086-2: 2011. Interestingly, no effects of phytotoxicity on Watercress were observed in this study (Table 1): all mixtures, including digestate, gave germination index values above 50%, which is commonly recognized as a threshold value for many crops (Zucconi et al., 1981).

In particular, all doses of mixtures and digestate gave a very similar germination value as the control samples (their difference compared to the germination of the control sample ranged from 5-7%), the most significant improvement in germination was achieved with a triple dose of digestate and haylage in a ratio of 10: 1. Similar results were obtained by Gell et al. (2011) and Sánchez et al. (2008), who evaluated digestive phytotoxicity on lettuce, radish, wheat and watercress.

Responses in terms of germination of seeds of Lepidium sativum can be used to evaluate toxic effects on plants, thus allowing the determination of the quality of waste through a simple assay (Zucconi et al., 1985). The toxic effects on plants are a combination of multiple factors (Zucconi et al., 1981).

Table 2 contains data on the coefficient of variation for the root length. It is valid that the larger the coefficient, the more the data differ from the average (the difference is again determined on the basis of the squares and its difference between the arithmetic average and the measured value). Here, too, it can be seen that the coefficients are relatively low, so in most tests we worked with a homogeneous set, which showed a relatively low variability of measured values.

In the case of determining the root length index according to EN 16086-2: 2012-01, the control sample is taken as the default value, which is assigned a value of 100%, for other mixtures it is then calculated and determined whether their lengths are greater (or shorter) than the root in the control sample. In general, we could say that the rule is that the longer the root, the better the fertilizing effect of the mixture. In our

Tab. 5. Germination indices of watercress phytotoxicity test Tab. 5. Wskaźniki kiełkowania testu fitotoksyczności rukwi wodnej

	10:1	5:1	3:1	Digestate	Control
lv (mm)	5.02	4.59	3.81	4.58	4.59
kv (%)	79.2	79.2	72	73.8	72
IK (%)	120.39	110.00	83.05	102.25	100.00

Tab. 6. Average elemental composition of the soil after the experiment Tab. 6. Przeciętny skład pierwiastkowy gleby po doświadczeniu

	units	10:1	5:1	3:1	Digestate	Control
рН		6.7	6.6	6.6	7.1	6.8
Calcium (Ca)	mg/kg of dry matter	300	284	268	336	256
Magnesium (Mg)	mg/kg of dry matter	38	36	36	33	31
Potassium (K)	mg/kg of dry matter	37	41	49	31	18
Sodium (Na)	mg/kg of dry matter	18	20	18	19	16
Exchange acidity (Al+H)	mmolchekv/ kg	<1	<1	<1	<1	<1
Ammonia nitrogen	mg/kg	1440	1410	1520	1280	1560
Total nitrogen	% of dry matter	0.15	0.17	0.18	0.14	0.16
Total organic carbon	% of dry matter	3.51	3.35	3.6	2.77	2.64

monitored samples, the root length index was above 100% for all examined samples (see Table 3).

In addition to the average root lengths, the Munoo-Liis vitality index (Table 4) also takes germination into account. Here, too, all the samples examined were above 100%. It again confirms that all the mixtures examined can be used as fertilizer. All mixtures showed increased germination compared to the control sample. In the case of digestate, we reached the same values as in the study of Maunuksel et al. (2012), which, in addition to pot tests with Chinese cabbage (Brassica pe-kinensis) and barrels, also performed germinating ten cress seeds (Lepidium sativum). No similar studies were found to compare other mixtures.

According to Table 5 of results of the germination index of tested samples from the watercress phytotoxicity test, samples 3: 1, digestate and haylage can be interpreted as well-mature "compost" and samples 10:1, 5:1 and digestate as compost with stimulating ability. All tested samples came out above 80%, which means that the fertilizing effect decreases and the effect of humus is stronger, i.e. that nutrients are more bound. Nitrogen and phosphate release is slower and nutrients do not leach into groundwater. All examined samples are therefore satisfactory from the point of view of the determined phytotoxicity on watercress germination.

The best ratio of germination indices was 10:1 with the resulting germination index of 120.39%. Another ratio is divided by a ratio of 5:1 with a separate with a germination index of 110%. Another digestion index, which was above 100%, was a digestate sample.

These results confirmed a study performed by Dimambr (2015), which showed that appropriately diluted digestate (in terms of NH_4 -N concentrations, pH and electrical conductivity) can generally achieve similar or higher yields compared to standard growing methods.

The most important indicators in the table are probably pH and ammoniacal nitrogen. When the pH rises above 6.5

some of the nutrients, micro-nutrients begin to precipitate out of the solution and can no longer be absorbed by the crop (Rush, 1987).

Hence for some horticultural crops reducing the pH below 7 is recommended, such as for hydroponic tomato (Neal and Wilkie, 2014), cucumber (Liedl, 2006) and lettuce production (Liedl, 2004b). At the same time a number of studies have highlighted the importance of considering the quantity of mineral N in digestates as this is the portion of N which is readily available to the crop (WRAP, 2012; Risberg, 2015). For horticultural purposes, a number of authors have highlighted the importance of matching the NH4-N concentration of the digestate to the crop requirements (Neal and Wilkie, 2014; Liedl, 2004a).

From this point of view, the values in the case of digestate appear to be the least suitable. As in the study according to Calamai (2020), all mixtures showed a significant increase in the content of secondary macronutrients (Ca, Na, K, Mg). The degree of alkaline saturation is an important indicator of agricultural soil quality. The value of this characteristic below 50% indicates a degraded soil (fertilisation, crop rotation), at the level of 50-75%, also agrotechnical errors, only values above 85% indicate a good physicochemical condition of the soil. As emphasised by Brodowski et al. (2005) and Cheng et al. (2006), this parameter plays a crucial role in the retention of water and nutrients for plants. Cation exchange capacity is important for maintaining adequate quantities of plant-available Ca, Mg, and K in soils. The applied fertilisation also influenced the share of cations in the sorption complex, generally decreasing the share of H+ ions and increasing slightly the share of Ca2+ ions and more clearly increasing the share of Mg²⁺ and K⁺ cations. The optimal Ca to Mg ratio should be 7:1 (Łabetowicz, 1999). According to Sanik et al. (1952), the Ca:Mg ratio has an impact on the solubility of cations in the soil solution. In our study, the ratio in the case of mixtures was in the range of 7.8-7.4:1, in contrast, in the case of digestate, the range was 10.1:1. The test results for the digestate are the same as for the research by Glowack et al. (2020).

Conclusion

In all cases of the examined samples of the determined test with watercress on Petri dishes, the growth of the root length was stimulated in comparison with the control growing media. From all statistically calculated quantities it can be deduced that all tested growing medias are in a positive position compared to the control growing media. Growing medias therefore have a positive effect on plant development. Based on chemical analyses of growing medias performed in the accredited laboratory Morava, the mixed growing medias can be characterized as growing medias with high nutrient content and heavy metal content meeting the limits for organic and livestock fertilizers according to EU regulation 2019/1009., On setting requirements for fertilizers, as amended. From the results of the watercress phytotoxicity test according to Plíva et al. (2006), it can again be deduced that the researched mixture matters are growing medias with fertilizing effects and can be used as fertilizer in all aspects. Due to the low homogeneity of the investigated growing medias, the results were

not objectively comparable, and therefore it is not possible to say unambiguously which mixture of the tested ratios was the most suitable for root growth and germination. However, all mixtures achieved a more significant improvement in the agrochemical properties of the soil compared to whole digestate fertilization. For a clear conclusion, it would be necessary to continue testing in a longer time horizon and in real conditions, such as in the case of a long-term experiment in Jaskulska et al. (2014) or Glowack (2020), who examined the impact of different agricultural practices on soil quality and yields.

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Badanie wpływu produktów odpadowych z biogazowni na kiełkowanie roślin i początkowy wzrost korzeni

Podczas produkcji biogazu fermentacja beztlenowa bogatego w składniki pokarmowe materiału roślinnego skutkuje powstaniem tzw. pofermentu. Zastosowanie materiału bogatego w składniki odżywcze obecnego w pofermencie może mieć działanie nawozowe, zwłaszcza dla intensywnie użytkowanych gleb rolniczych oraz dla plonów, może wpływać na cykl składników odżywczych.

Celem artykułu jest przedstawienie możliwości wykorzystania mieszanki pofermentu i sianokiszonki (wykorzystanie efektu nawozowego obu substancji), a jednocześnie przyczynienie się do poprawy właściwości agrochemicznych gleby.

W pracy oceniono wpływ zastosowania mieszanki pofermentu i sianokiszonki na kiełkowanie i wczesne etapy rozwoju roślin. Artykuł dotyczy podstawowych mieszanek testowych pofermentu i sianokiszonki w proporcjach 10:1, 5:1 i 3:1 i porównuje wyniki z zastosowaniem całego pofermentu. Uproszczone statystycznie obliczone ilości wykazały, że wszystkie badane mieszanki mają lepsze działanie nawozowe w porównaniu z kontrolnymi podłożami uprawowymi. Na podstawie analizy chemicznej podłoży uprawowych zbadano podłoża uprawowe z mieszaniną pofermentu i sianokiszonki, charakteryzujące się jako podłoża uprawowe o wysokiej zawartości składników odżywczych i niskiej zawartości metali niebezpiecznych. Badane podłoża uprawowe spełniały tym samym limity dla nawozów organicznych i komercyjnych. Nawozowe efekty podłoży uprawowych mieszanką pofermentu i sianokiszonki można również zauważyć na zwiększenie udziału makroskładników w glebie, ograniczając nawożenie tylko w samym pofermencie.

Słowa kluczowe: poferment, kiełkowanie, sianokiszonka, gleba, szalki Petriego, stacja biogazowa, odczyn pH



Assessing the Real Risk of Mining Industry Environmental Impact. Case Study

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Abstract

The aim of this article is to analyse the real risk that mining operations pose to the environment, including all the main concerns related to the project's planned operations and their environmental impacts. In order to carry out an in-depth analysis of a practical case involving the real process of mineral extraction, we use the Analytic Hierarchy Process (AHP) and Leopold matrix as a method of measurement. The subject of the investigation is the extraction of lithium from natural brine located in South America's so-called Lithium Triangle, in the geographical limits of Argentina, Bolivia and Chile, where more than 80% of the world's lithium reserves are located. The case study showed that the elements of the environment most exposed to mining activities are the biosphere, lithosphere and hydrosphere. The vast areas of the mining company are covered by sedimentary ponds with brine. Pumping the brine to the surface results in a loss of groundwater resources and, consequently, changes the water cycle in the catchment area. The habitats of aquatic and terrestrial fauna and flora are significantly changed or irretrievably damaged.

Keywords: mining activities, lithium, environment, AHP, Leopold matrix

Introduction

Mining and metallurgic industries are one of the most influential pillars of the economy; not only do they satisfy material needs of the industrialized world, but they also ensure and support the growth of developing countries. Materials and products consumed by the countries, especially those which are still developing their economy and basic needs, are provided directly or indirectly through their extraction by the mining sector from the natural environment. Mining is also considered to play an important role in the economy at a local level due to a growing number of investment projects and job opportunities on the market [1]. Extracting and exploiting its own mineral resources is a very profitable option for a country to boost its economy whenever the treatment and transformation to consumer goods is not possible or not efficient enough [2,3]. On the other hand, mining has a very negative image from the social and cultural point of view as it is associated to high contamination level and degradation of the biosphere due to the uncontrolled human activity and its adverse effects on the environment. These socio-cultural attitudes cannot be ignored and must be looked at closely to help the industry develop and change its negative image [4]. It is necessary to point out that even though the preservation of the environment is a crucial and very important aspect, it is not the only factor that determines the social acceptance of the extractive industry. On many occasions both parties (mining corporations and social communities) see a mutual interest. This applies to land acquisition, payments for the use of water, presence of subcontractors, compensation, local purchases, social investment strategies, etc. In order for mining to become socially acceptable, it is important not to overlook the initiation of measures at legislative level, the effective

implementation of measures to protect against the effects of mining activities and ethical motivation when designing the processes involved. The biosphere is intrinsically exposed to the effects of mining activities, therefore every mining project must take into consideration the management of the effects they cause to the environment, starting with design and business decisions. The industry must ensure that the environment is protected; it needs to be the main step in a typical cycle of mining activities (prospecting/exploration, development, mineral extraction, metallurgic process and closure/ reclamation) [1,5-7].

Argentina, Bolivia, and Chile have approximately 75% of the world's lithium brine reserves in the area known as the lithium triangle. Currently, lithium can be extracted from three different types of deposits: brine (as in Chile, Bolivia and Argentina), pegmatite (hard rock) and sedimentary deposits, each requiring different types of extraction and processing methods. Today, the first two types are the most commonly used for commercial lithium production. Lithium is used in a variety of products and in different industrial areas; more traditional uses include applications in ceramics, glass and medicine [8,9]. More recent areas of use include applications such as lithium-ion batteries used in small electronic devices, or larger batteries used in electric and hybrid cars. Future uses include the production of nuclear energy through nuclear fusion, an area currently under investigation.

The process for converting brine to high-purity lithium carbonate follows industry standards: pumping brine from the salar (salt flat), concentrating the brine through evaporation ponds and taking the brine concentrate through a hydrometallurgical facility to produce high-grade lithium carbonate. The basic process inputs include evaporated brine, water,

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Fig. 1. Location of the mine (Source: own study based on https://mapcarta.com) Rys. 1. Lokalizacja kopalni (Źródło: opracowanie własne na podstawie https://mapcarta.com)

lime, soda ash, HCl, NaOH, and natural gas. The evaporation ponds produce salt tailings composed of Na, Mg, Ca, K, and borate salts. The brine concentrate from the terminal evaporation pond is further processed, through a series of polishing and impurity removal steps [10]. Soda ash is then added with the purified brine concentrate to produce lithium carbonate that is dried, micronized, and packaged for shipping. The lithium recovery process consists of the following main processing stages: brine production from wells, sequential solar evaporation, pond-based impurity reduction by liming, plant-based impurity polishing, lithium carbonate precipitation, mother liquor treatment and recycle, lithium carbonate crystal compaction and micronization, lithium carbonate packaging [11,12].

The current process design, based on testing and simulation, has been enhanced with: pond-based sulphate and boron reduction, plant-based potassium chloride reduction, mother liquor re-concentration. Then the brine is pumped from the salar into the pond system. As it progresses through the ponds, different salts precipitate, and chemical treatments are applied [13].

Study case

Location of the mine

The case under study is the production of lithium carbonate by Lithium Americas at the Cauchari and Olaroz Salars, located in the Jujuy province, in the Department of Susques, north-western Argentina. The nearest port is Antofagasta in Chile located 530 km to the west of the salars by road. The salars are located in the area known as "Lithium Triangle", which refers to the territory shared by Chile, Argentina and Bolivia, where more than three quarters of the world 's lithium supply is entrapped underneath their salt-rich soil. In desert climates lithium brines are formed due to a slow inflow of lithium, other metals and salts; since there is no outflow, gradual evaporation over long periods of time (thousands of years) slowly increases lithium concentrations to an economic level [14].

The lithium is extracted from the brine under the surface. The brine is contained within the pore space of alluvial, lacustrine, and evaporite deposits that have accumulated as a multi-layer aquifer in the structural basin of the salars. The brines from Cauchari are saturated in sodium chloride with total dissolved solids on the order of 27% (324 to 335 grams per litter) and an average density of about 1.215 grams per cubic centimetre. The other primary components of these brines include potassium, lithium, magnesium, calcium, sulphate, HCO₃, and boron as borates and free H₃BO₃ [15-17].

Materials and Methods Methods Description

To evaluate and analyse the environmental impact of the subject mine we apply the AHP and Leopold Matrix principles and techniques. The AHP acronym stands for Analytic Hierarchy Process and is a multi-criteria decision making method. It translates the value of the impacts into measurable numeric relations. The main characteristic of the method is the use of pairwise comparisons; in our case we compare the impact on different elements of the environment one by one, pair by pair, in order to create a hierarchy showing the importance of the impact on different elements (biosphere, atmosphere, lithosphere...), giving a reasonable explanation to every comparison [18,19].

There are various stages involved in the process: 1. Structure the multi-criteria problem in order to solve it in the form of a hierarchy by decomposing the general task into smaller and simpler components. The hierarchical structure can be shown as a pyramid where the summit hosts the main task, in this case "Assessment of the environmental impact of the mine"; 2. Design priorities to all of the components in the structure by assigning factor weights from 1 to 9 (table 1); then all the elements are compared and evaluated in pairs in order to specify their importance and find the most relevant element to achieve the main task; 3. This stage aims at verifying the pairwise comparisons of each element. An advantage of using this hierarchical method is that errors are limited; 4. Designation of priorities through weights assigned to different possibilities, classification of those possibilities, and their assessment in relation to their priority of implementation. Finally the analysed hierarchical model is completed, with a classification of priority vectors in the order of priority: the higher the value of the vector the more important the element is. By means of that model we can evaluate the whole project to make the best choices before starting any investment process [20,21].

With the weights assigned to each element obtained from the AHP method, we proceed to the construction of a Leopold matrix. In this case we use balanced weights calculated by experts in the field. These weights represent the general hierarchical importance of the environmental elements affected by the mining project [20,23].

Tab. 1. Scale of degrees of preference for paired comparisons in the AHP method [22]Tab. 1. Skala stopni preferencji dla porównań parami w metodzie AHP [22]

Degree of importance	Definition				
1	The elements (features) are equally important				
3	A domination one element over other (second) is minimal				
5	A domination one element over other (second) is medium				
7	A domination one element over other (second) is big				
9	A domination one element over other (second) is very big				
2, 4, 6, 8	Indirect value between odd values				

Tab. 2. Leopold matrix results (Source: own study) Tab. 2. Wyniki macierzy Leopolda (Źródło: opracowanie własne)

		Environmental elements *							
The impact of the mine on	Action	L_sph	H_sph	At_sph	An_sph	B_sph	V_to_nh	Sum	
the environment	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		1		Importan	ce	I	1	
		0,261	0,194	0,059	0,046	0,29	0,151	1,0	
Occupation	Magnitude of impact	2	0	0	0	1	0	3	
of Surface	Impact of action	0,522	0	0	0	0,228	0	0,75	
Defensetation	Magnitude of impact	0	0	0	0	0	0	0	
Derorestation	Impact of action	0	0	0	0	0	0	0	
Infrastructure	Magnitude of impact	1	0	2	0	0	0	3	
of power plant	Impact of action	0,261	0	0,118	0	0	0	0,379	
Noise and	Magnitude of impact	0	0	0	0	1	0	1	
Vibration	Impact of action	0	0	0	0	0,228	0	0,228	
Water in the	Magnitude of impact	0	5	0	4	4	1	14	
manufacturing	Impact of action	0	0,97	0	0,184	0,912	0,151	2,217	
Reclamation	Magnitude of impact	0	0	0	0	0	0	0	
Activities	Impact of action	0	0	0	0	0	0	0	
Municipal	Magnitude of impact	2	0	2	0	1	0	5	
Wastes	Impact of action	0,522	0		0,118	0	0,228	0,868	
Industrial Wastes	Magnitude of impact	3	2	0	0	1	0	6	
	Impact of action	0,783	0,388	0	0	0,228	0	1,399	
Unpleasant Odors	Magnitude of impact	0	0	0	0	1	0	1	
	Impact of action	0	0	0	0	0,228	0	0,228	
Pollutant emissions to the air	Magnitude of impact	0	0	2	1	1	0	4	
	Impact of action	0	0	0,118	0,046	0,228	0	0,392	
Sum of Impact of action		2,088	1,358	0,236	0,348	2,052	0,379	6,461	

* L sph – Lithosphere; H sph – H ydrosphere; At sph – A tmosphere; An sph – A ntroposphere; B sph – B isophere; V to nh - Vulnerability to natural hazards environment



Fig. 2. Leopold actions results (Source: own study) Rys. 2. Wyniki matrycy Leopolda (Źródło: opracowanie własne)



Fig. 3. Wind Rose. Leopold Elements Results (Source: own study) Tab. 3. Róża wiatrów. Wyniki matrycy Leopolda (Źródło: opracowanie własne)

The Leopold matrix is a framework method that enables us to do the environmental risk assessment of a project, on the basis of criteria related to significance, probability, and duration of the impact. Similarly to the AHP, it belongs to the multi-criteria decision making methodology. It consists of a two-dimensional matrix where individual actions are assessed in relation to the actual environmental features and conditions that could be affected by the project's operations. In this method we use the weights obtained in the AHP as a reference in order to assess the actions that accompany the extractive activities and affect each element, so that we are able to create a specific hierarchy of elements affected and specify actions taking place within the scope of the mining project subject of the study [24,25].

AHP Analysis Method

The main task of the analysis is the assessment of the environmental impact of the Cauchari-Olaroz project. The items subjected to priority analysis are the impacts on the following parts of the environment: lithosphere (solid, outer part of the earth), atmosphere (mixture of gases surrounding the earth), hydrosphere (all of the water, ice, and water vapour at or near the surface, such as the seas, clouds, and the water in and under the ground), biosphere (all type of life present), anthroposphere (part of the environment occupied, made or modified by humans for use in human activities and human habitats), vulnerability to natural hazards (natural physical phenomena caused by a fast or slow chain of events: earthquakes, landslides, tsunamis, extreme temperatures, etc.).

The analysis of the environmental impact of mining industry was carried out with the participation of experts selected according to their competences, which allowed to include all the elements needed to assess the analysed problem. The evaluations presented in the paper (pairwise comparisons with criteria and subcriteria based on a rating scale from 1 to 9, the so-called Saaty scale) were carried out as part of a group decision making process, the so-called brainstorming. The authors of the paper were personally involved in the brainstorming session, and experts were selected from various fields of science: geology (7 mining geologists), mining (5 mining engineers), environmental management and engineering (4 experts), environmental protection (5 experts), ecology (2 experts). In total, 23 experts participated in the valuation of the models.

The valuations obtained were presented in the form of local weights (importance). The weight with a value close to zero means a small amount of impact. The weight close to 1 indicates a strong impact of the project on a given item. The sum of weights at each level is 1 (100%). The results are as follows: lithosphere 0.26; hydrosphere 0.19; atmosphere 0.06; anthroposphere 0.05; biosphere 0.29; vulnerability to natural hazards 0.15.

Each number represents a vector corresponding to the priority percentage of every element in the overall scheme: the higher the value of the vector the more important the item is [18,20].

Leopold Matrix Method

As explained earlier, the weights are used to create a Leopold matrix with the following results (table). With the data obtained from the AHP matrix we obtain the hierarchies of various elements of the environment affected by the mining project and actions having an impact on the environment. The elaboration of a Leopold matrix consists in identifying all the activities (actions) accompanying the operation of the mining project and in placing them in columns. For each activity, we use a rating (magnitude of impact) on a scale from 0 (no impact) to 5 (very strong impact). By multiplying the magnitude of impact and weights (importance) of environmental elements and by summing all the impacts, the total value of the mine's environmental impact is obtained [24,25].

Results and Discussion The Actions Analysis

The action having a major impact on the environment is by far "Pumping industrial water" (2,217) since the principal method of lithium extraction consists in pumping underground brine into the surface and filter it through different stages of evaporation and precipitation until getting the final highly-concentrated lithium carbonate that can be subjected to further processing. All this procedure has crucial impacts on the surrounding hydrosphere (Fig. 2).

Pumping large amounts of water, both brine and fresh water, for the production of lithium carbonate, interferes with groundwater networks and carries the risk of changing water flows and drawing down the water table. The plains or bogs and the lake bodies are affected by the exploitation of groundwater by mining companies. These activities alter the water cycle of the basin, prevent water recharge, lower the phreatic levels, reduce the flow of the slopes, dissect the surfaces of the plains, reduce the levels and surfaces of the lake bodies.

Given the importance of groundwater to both surface water sources and wildlife and human habitats, water resources alteration may be considered as having some social and economic impact on local communities and their overall wellbeing [1].

Plants are highly dependent on water availability and even minor changes in the water budget can result in dramatic increases or decreases in vegetation. On the other hand, the most important habitats for both flora and fauna are the arid wetlands which are less dependent on precipitation but more on the availability of groundwater.

Another item in the hierarchy with high influence on the environment is "Production of Industrial Wastes" (1,399). Water is considered to be the main industrial waste product in the process of lithium processing. It has the risk of contaminating the lithosphere through leakage and drainage from leaching piles, processing ponds and tailing liquids disposal because at some stages of brine processing the brine shall be acidified with hydrochloric acid and reach a pH of between 3 and 4, with the risk of acid leakage. This industrial water can pollute underground water beneath the facilities and surface water that receive their discharge water. Toxic compounds are likely to leak from these facilities, pass through the ground and affect underground water, especially if the bottom of the facility has not been protected with a waterproofing liner.

Waste from the evaporation process in the ponds leave high amounts of salts accumulated on the bottom of the ponds. These salt piles may reach 15 m in height. Estimations indicate that approximately 740 ha of salt piles will be built over a 40-year period and these piles will be built near the pond areas. These accumulated salts are classified as inert waste. The salts are generated from brines already present in the salar and do not introduce foreign compounds. It is estimated that sodium chloride and sulphate make up over 87% of this waste.

Actions considered to have a lesser impact on the environment are "Production of Municipal Waste" (0,868) and "Use of land" (0,75). Municipal waste produced by the workers and people arriving to the facilities is inherent to every place where human activity is present. Several potential effects are the consumption of energy and materials used to make packaging and products that are discarded later. Surface water is polluted by garbage thrown away into wetlands, ponds, and pipes. In places where garbage is concentrated, leachates drain and contaminate underground water. Soil pollution is another potential effect. The presence of oils, greases, heavy metals and acids, among other contaminating residues, alter physical, chemical and fertility properties of the soils. Air pollution is also a potential effect: municipal solid waste left in open dumps deteriorates the quality of the air we breathe, both locally and in the surroundings, because of burns and fumes that reduce visibility; dust raised by the wind in dry periods can transport harmful microorganisms to other places, causing respiratory infections and nasal and eye irritations. Degradation of organic matter present in waste produces a mixture of gases composed mainly of methane and carbon dioxide (CH₄ and CO₅) recognized as greenhouse gases (GHGs) that contribute to climate change.

Land use represents a relevant item. The ponds cover a large land: the total evaporation area required for the production of 40,000 tpa of lithium carbonate is 1,200 ha when including consideration for harvesting of salt deposited in the ponds. Although the excavation is only superficial, the fact of occupying a large part of land should be considered as an alteration of the environmental conditions, namely the Earth's crust. The excavation will need to be refilled and recovered afterwards, which is much easier than in the case of underground or open pit mining. Using a large portion of land can affect some living beings and alter their habitat. However, since there is plenty of land available for their living, the effect would be just a temporary migration of some of them to other areas. When the project comes to its end, the recovery of the habitat for plants and animals must be ensured, which - as mentioned previously - is less labour-intensive and easier than in the case of other extractive methods.

Other items included in the hierarchy with low environmental impact are "Pollutant emissions to the air" (0,392) and "Infrastructure of Power Plants" (0,379). Air pollutants are low in quantity as they are produced by diesel equipment. In comparison with open pit mining or underground mining, their impact is very low and has no high significance with one exception: the development stages of the project where more machinery is needed. The emissions from the power plant servicing the project are also low since the plant is totally powered by natural gas whose CO_2 emissions are low and with no high significance compared with diesel and oil. In addition, there are backup diesel generators used in case of emergency. The infrastructure of the power plants does not affect the environment significantly, either. The habitat area they occupy is not highly altered, nor substantially affected.

Other items with none or almost none impact on the environment are "Noise and vibration" (0,228), "Unpleasant odours" (0,228), "Reclamation activities" (0) and "Deforestation" (0). There is little noise and vibration as there is no blasting needed and a few machines are used. There are no other unpleasant odours but the ones from some salt in the ponds that might affect some living beings but with no significance in the overall scheme. Reclamation activities have no influence, and as the territory is a dry area, there is no deforestation carried on.

The Elements analysis

As we can see in Figure 4, the most affected part of the environment is the biosphere (2,28) highly impacted as a consequence of altered hydrosphere. Due to a large number of springs, the wetlands occupy an important area and are essential for camelid farming.

The groundwater system forms an internal tissue that regulates external soil moisture, which is reflected in the formation of springs, slopes, rivers, pools, lagoons and wetlands that serve as a habitat for avifauna and human populations settled in the region.

The greatest concern usually lies with the extraction of fresh water since it is necessary not only for human life but also for the plains, i.e. flora and fauna on the surface. Similarly, the extraction of brine – which is much higher – can adversely affect fresh water layers. The extraction of groundwater can result in habitat alteration for terrestrial vegetation and flora, fauna and aquatic fauna. Wildlife (e.g. birds) dependent on ponds and wetlands could be particularly affected, and camel flocks dependent on wetlands could be reduced or disappear locally.

The greatest concern is the cumulative, permanent and irreversible nature of brine extraction because the reservoir will gradually diminish and extraction will not allow a return to the original conditions. The brine levels, in turn, will be recovering for a very long period of time (geologic time). There are other potential impacts of adverse events that could contaminate the biosphere, namely the potential pollution of the soil due to leaking, waste, noise and vibration from machinery which could to some extent affect the lives of the surrounding living beings.

Next hierarchical item affected by the project is the lithosphere (2,088). It has reached a very high impact level in the overall scheme because of the accumulation of several potential impacts. The main action showing the highest impact is pumping industrial water. As brine extraction is basically focused on pumping underground water, there is little alteration made to Earth's crust: a superficial excavation to create the ponds where the water is pumped; punctual drillings to create the pumping systems; roads built to facilitate the access to the area; and in some parts the surface was altered by the construction of buildings and facilities. The impact of these factors on the environment and in the overall scheme is neither serious nor permanent.

The ponds are lined with a multi-layer liner made of a polymer-based material and engineered granular bedding so that insulation is assured and filtration to the ground is avoided. Using a large portion of land can affect some living beings and alter their habitat. However, since there is plenty of land available for their living, the effect would be just a temporary migration of some of them to other areas. When the project comes to its end, the recovery of the habitat for plants and animals must be ensured, which – as mentioned previously – is less labour-intensive and easier than in the case of other extractive methods. Also, different types of waste have a high potential for contaminating the lithosphere. Municipal waste can lead to soil pollution.

Next item of the hierarchy to bear the project's impacts is the hydrosphere (1,358). Pumping immense amounts of brine to the surface not only lowers the brine level, but also depresses fresh groundwater in the basin. There is the risk of degrading the locally formed meadows and lagoons being an essential water resource to the region. It is considered that 80% of the water, so-called "fossil water" will not be renewed with contemporary rainfall because it originated in much more humid climatic conditions. As the modern water recharge is very limited, water may rise very slowly or the place may be even considered as a non-renewable water resource. Given the aridity of the area, which is insufficient to recharge the water aquifers, which in many cases are of non-renewable origin, and the possible impact that the extraction of brine and water has on the water table, extraction levels should be of major concern and must be consistently overviewed.

Waste water as industrial waste has the risk of contaminating the lithosphere. When it comes to municipal waste, surface water is polluted by garbage discarded into the wetlands, ponds and pipes. In places where garbage is concentrated, leachates are filtered out and contaminate the underground water.

Next element of the hierarchy to be affected to a small extent is the atmosphere (0,354). The main pollutants are sand and gravel because of the excavations and transport taking place before the construction of access roads; then there are greenhouse gases (CO2) emitted by diesel equipment and transport vehicles. However, all these factors were only temporary and had their impact at the stage of building the facility and infrastructure. Nonetheless, even at that time their environmental impact was not significant.

In the operational phase of the project, there are still emissions from diesel vehicles reaching the area, but they have a small environmental impact because the need for transport to the zone is very low due to a small number of workers required to the project. The plant includes a diesel storage and dispensing station for mobile equipment and transport vehicles. Diesel fuel will also be used in stand-by generators and back up for dryers in the plant. The equipment will be mainly fuelled with natural gas obtained from the Rosario gas compression station which is on the Gas Atacama pipeline, 52 km north of the project site.

The anthroposphere (0,23) is least affected item despite the fact that local communities are trying to express their opposition through the media. Given the importance of groundwater to both surface water sources and wildlife and human habitats, water resources alteration may be considered as having some social and economic impact on local communities and their overall wellbeing.

The population near the territory consists of relatively small and dispersed groupings, often suffering from poor infrastructure and high rates of material poverty. They are characterized by a close relationship with the natural environment, and their integrity and reproduction depend on nature, given that their main form of economic support is livestock or agriculture, and nature around the ecosystem forms part of their cultural heritage. However, they do not live in isolation, nor outside the market economy, since they not only use the products of these activities for sale or barter with other regional products, but also complement their livelihood with wage work in mining or tourism. Finally, they have or aspire to legal recognition of indigenous territories with community control over land and natural resources. The socio-economic and cultural impacts on the local population whose main activity is camelid farming based on the bogs, and whose culture is closely related to water is one of the main concerns. Also the disappearance or degradation of drinkable water sources (wells and springs) located near the points of lithium extraction, or coming from the same aquifers is going to affect drinkable water supplies.

In the early phases of the project some conflicts arouse between local communities and companies because the latter failed to provide information to local representatives [1].

Another important socio-economic aspect is that even though companies usually claim that in the long term their projects are going to generate employment and capacity for the community, the experience so far shows that lithium mining itself generates very few jobs in the mining regions since conventional evaporation technology is not very labour-intensive. About 500 workers are usually needed for the construction of industrial plants while during production the number decreases to about 200 people with little involvement of local employees [2].

When national or sub-national states fail to comply with established laws such as the right to consultation and participation, local communities lose control over the territory without their consent. This is reflected in the fact that local populations have little access to concrete information about projects and are characterized by uncertainty, sharing concerns about water, the resource by which their main productive activities depend on [3].

The last item with very little impact and no significance in the overall scheme is vulnerability to natural hazards (0,151). The only probable potential risk is the appearance of torrential rainfall events in the wet season that could cause the ponds to overflow.

Conclusions

Mining for the mineral puts pressure on the environment. The scale of the transformation of the environment depends on the area occupied, the location of the deposit within the natural habitat, and the sensitivity of the species to changes in nature. During the exploitation of deposits, the relief of the land is strongly transformed, the soil cover and vegetation are removed, and adverse erosion processes occur. Mining operations have a significant impact on the landscape of the surrounding areas [23].

Some stages of exploitation are very burdensome for the environment. At the preparatory stage, the overburden is removed, vegetation is destroyed and the land is prepared for exploitation. The natural habitats are irretrievably destroyed and the vegetation undergoes degradation. Some animal species lose their habitats and others, deterred by the noise of working equipment, move to other places. The study case concerning the extraction of brine and its processing into high-purity lithium carbonate by Lithium Americas at the Cauchari and Olaroz Salars showed that it is the hydrosphere that is most affected by these operations. Pumping the brine to the surface on an industrial scale disturbs the balance of water bodies. As a result, the groundwater table is drawn down and resources in surface reservoirs are depleted. The exploitation of water requires careful analysis in order to eliminate or mitigate negative effects on ecosystems. The availability of groundwater is a prerequisite for the occurrence of flora, terrestrial and aquatic fauna habitats. Even small changes in the water balance can cause a dramatic decline in plant vegetation [10].

The Cauchari and Olaroz Salars cover a large area of land, which should be regarded as a transformation of the earth's crust. A large part of the lithosphere is covered by evaporative ponds. Leakage and drainage from ponds and tailing liquids disposal are a source of lithospheric pollution. Soil contamination by heavy metals, acids and grease contained in municipal waste is observed. Once the mineral has been used, plant and animal habitats will need to be restored and rehabilitated.

The paper demonstrated that processing the brine into lithium carbonate at the Olaroz Salars has negative consequences. However, as long as the mining is carried out correctly, in a manner consistent with the idea of sustainable development, and the rehabilitation is carried out in the right direction, it can bring many benefits for people and the environment [26]. The positive impact of mining is reflected in the creation of new habitats for plants and animals in the post-mining areas and in landscape diversification activities.

Author Contributions

Conceptualization: W.S., K.C. and E.S.; methodology, W.S.; formal analysis: W.S.; investigations: K.C.; writing original draft preparation: E.S., W.S. and K.C.; writing - review and editing: W.S., E.S. and K.C.; visualization: E.S. and K.C.; supervision: W.S. Authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest

The authors declare no conflict of interest.

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Ocena rzeczywistego ryzyka oddziaływania przemysłu wydobywczego na środowisko. Studium przypadku

Celem artykułu jest analiza rzeczywistego ryzyka, jakie eksploatacja górnicza stwarza dla środowiska, z uwzględnieniem wszystkich głównych czynników związanych z planowanymi działaniami w projekcie i ich oddziaływaniem na środowisko.

W celu przeprowadzenia dogłębnej analizy przypadku praktycznego dotyczącego rzeczywistego procesu wydobycia minerałów, jako metody pomiaru wykorzystano Analytic Hierarchy Process (AHP) – wielokryterialnaą metodę hierarchicznej analizy problemów decyzyjnych oraz macierz Leopolda.

Przedmiotem badań jest eksploatacja litu z naturalnej solanki znajdującej się w tzw. Trójkącie Litowym Ameryki Południowej, w granicach geograficznych Argentyny, Boliwii i Chile, gdzie znajduję się ponad 80% światowych zasobów litu. Studium przypadku wykazało, że elementami środowiska najbardziej narażonymi na działalność górniczą są biosfera, litosfera i hydrosfera. Rozległe tereny przedsiębiorstwa górniczego pokrywają stawy osadowe z solanką. Wypompowanie solanki na powierzchnię powoduje utratę zasobów wód podziemnych i w konsekwencji zmianę obiegu wody w zlewni. Siedliska fauny i flory wodnej i lądowej ulegają znacznym zmianom lub nieodwracalnym uszkodzeniom.

Słowa kluczowe: działalność górnicza, lit, środowisko, AHP, macierz Leopolda



Extraction of Selected Metals from Waste Printed Circuit Boards by Bioleaching Acidophilic Bacteria

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Abstract

Technological innovations and increased demand for electronic devices resulted in production of more and more waste with high metal content. Worldwide, 50 million tons of WEEE (Waste from Electrical and Electronic Equipment) are generated each year. Given the metal content present in electrical waste (e-waste), it is considered to be an urban mine and, if properly treated, can serve as an alternative secondary source of metals. Waste printed circuit boards (WPCBs) that constitute approx. 3-5% of WEEE by weight are of particular importance. They contain, on average, 30-40% of metals by weight, with higher purity than in minerals. With environmental and economic benefits in mind, increasing attention is being paid to the development of processes to recover metals and other valuable materials from WPCBs. The research presented in the article aimed at assessing the usefulness of the biotechnological method for leaching of selected metals from e-waste. The results indicate that it is possible to mobilize metals from WPCBs using microorganisms such as Acidithiobacillus ferroxidans bacteria.

Keywords: Acidithiobacillus ferrooxidans, bioleaching, waste printed circuit boards, WPCBs

Introduction

Innovation in today's economy is increasingly dependent on non-ferrous metals: copper, nickel, silver, lead and others, and rare earth elements (REEs). Alternative power engineering is one of those industries where the consumption of critical and strategic raw materials will grow exponentially in the coming years. Securing stable sources of supply is therefore becoming not only critical to Europe's economic success, but also to its green aspirations and the transition it brings about from an economy dependent on fossil fuels to one based on renewable sources. Growing demand for non-ferrous metals over the past centuries has put constant pressure on natural resources - many of the important and most widely used raw materials that are running out, deposits of readily available and high quality are available. What is more, the extraction and processing of non-renewable raw materials involves interference in the environment (Pollmann et al., 2018; Hołda and Krawczykowska, 2020).

A relevant approach concerning saving resources seems to be recycling. It allows for reusing raw material that has already been exhausted. Waste produced becomes a renewable, secondary source of natural resources which limits its depletion. Moreover, effective recycling provides safe resources for industrialised countries and reduces dependence on resource-rich countries (Hołda and Krawczykowska, 2020).

Currently, the highest growth rate is attributed to WEEE (Waste from Electrical and Electronic Equipment). This is due to the increase in consumer demand for electronics and the affordability and shortened lifespan of electrical and electronic products. Worldwide, 50 million tons of WEEE waste are generated each year, but only less than 20% of it is recycled (Xia et al., 2018; Sethurajan and Gaydardzhiev, 2021). Given the metal content present in electrical waste (e-waste), it is considered to be an urban mine and, if properly treated, can

serve as an alternative secondary source of metals. Continuous innovation of consumer EEE results in highly variable material properties and shape of end products, with increasing complexity. So the elemental composition of the waste is also highly variable and complex. Waste printed circuit boards (WPCBs) that constitute approx. 3-5% of WEEE by weight are of particular importance. They contain, on average, 30-40% of metals by weight, with higher purity than in minerals, including base metals (Cu, Zn), precious metals (Au, Ag, Pd) and heavy metals (Isildar et al., 2019, Khatri et al., 2018; Garg et al., 2019; Tipre et al., 2021). However, the percentage of reuse and recovery of the precious components contained in the WPCB is very low. With environmental and economic benefits in mind, increasing attention is being paid to the development of processes to recover metals and other valuable materials from WPCBs.

Conventional technologies including mechanical and chemical methods can be used to extract metal from e-waste. However, WPCB recycling processes by pyrometallurgical or hydrometallurgical methods generate atmospheric pollution due to the release of dioxins and furans, and generate large amounts of wastewater. Moreover, such processes are costly due to high energy consumption and should not be considered the most economical way to extract valuable components from WPCBs (Zhang et al., 2012; Hao et al., 2020; Kaya 2017; Li et al., 2018; Lu and Xu, 2016; Akcil et al., 2015; Cui and Zhang, 2018; Bosecker, 2006; Krebs et al., 2006). Therefore, it seems that biohydrometallurgical methods which can be described as ecological, inexpensive, "low-tech" processes with low emission of hazardous substances, using naturally occurring microorganisms and their metabolic products to extract metals from the matrix, have a chance to be applied on an industrial scale. These methods have already been successful in the processing of low-quality ores and bioleaching of in-



Fig. 1. Oxidation/reduction reactions carried out by A. ferrooxidans (Quatrini and Johnson, 2019) Rys. 1. Reakcje utleniania/redukcji z udziałem bakterii A. ferrooxidans (Quatrini and Johnson, 2019)

dustrial solid waste (Xia et al., 2018; Pollmann et al., 2018; Zhuang et al., 2015; Awashti et al., 2019). The applicability of bacteria in the extraction of metallic elements from waste is directly related to their participation in the biogeochemical cycle of metals in the environment. Obviously, important factors influencing the transition of metals from insoluble to soluble forms are abiotic factors such as pH, oxidoreduction potential, ionic strength or form of metal occurrence, but in addition to important physico-chemical conditions, biotic factors play an important role. Among them, the microorganisms capable of easily adapting to extreme conditions (high concentrations of heavy metals) and of using metals as a source of energy or as final electron acceptors are the most important. It is the by-products of bacterial metabolic processes (energy-transducing processes) such as ferric iron ions (ferric iron) and sulfuric acid(VI) that mobilize metals in the environment, including toxic metals (Valdes et al., 2008).

The microorganisms involved in the process of bioleaching of WPCBs are mainly chemoautothrops Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans (Brandl et al., 2001; Hong and Valix, 2014; Yang et al., 2014; Wilner and Fornalczyk, 2013; Blazek et al., 2012), iron-oxidizing bacteria and sulfur bacteria (Wang et al., 2016; Karwowska et al., 2014; Xia et al., 2017; Willscher et al., 2007; Shah et al., 2015; Ilyas et al., 2010; Xiang et al., 2010; Zhu et al., 2011) heterotrophic bacteria Chromobacterium violaceum (Faramarzi et al., 2004; Chi et al., 2011) and mould fungus Aspergillus niger (Jadhav et al., 2016; Brandl et al., 2001; Faraji et al., 2018; Kolenčík et al., 2013; Hołda and Krawczykowska, 2020), Penicillium sp. (Ilyas and Lee, 2013; Brandl et al., 2001) and Rhizopus sp. (Netpae and Suckley, 2019).

Mesophilic Acidithiobacillus ferrooxidans bacteria were used for the study presented in this paper due to their extremely extensive metabolic capabilities (Fig. 1). They are extreme and obligatory acidophiles, deriving chemiosmotic energy from the naturally occurring large transmembrane pH gradient (extracellular pH typically 1.5-3.0 and intracellular pH - 6.5). Most strains grow optimally at pH 2 and have a minimum growth pH of 1.3. As chemolithoautotrophic organisms, they use only inorganic electron donors: reduced and elemental sulfur, iron (Fe²⁺) and hydrogen (H₂). On the other hand, the electron acceptor can be either molecular oxygen or iron or sulfur which converts these bacteria into facultative anaerobes (Quatrini and Johnson, 2019).

Mechanism of bacterial bioleaching

Biological leaching of metals is carried out by a wide variety of microorganisms comprising three mainly groups

- chemolithotrophic prokaryotes,
- heterotrophic bacteria,
- microfungi.

Many different chemolithotrophic and organotrophic microorganisms are involved in the bioleaching of ores. For the recovery of metals from WEEE through biotechnology, studies have used both autotrophic and heterotrophic organisms. However, the fundamentally different chemistry of metals contained in sulfide ores relative to WEEE implies differences in leaching mechanisms (Isildar et al., 2019). Fig. 2 provides an overview of conventional autotrophic bioleaching of sulfide ores and heterotrophic and autotrophic bioleaching of recyclables.

Autotrophic bioleaching of WEEE

Chemolithoautotrophic organisms (mesophilic Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans and Leptospirillum ferrooxidans and thermophilic Acidianus brierleyi, Sulfobacillus thermosulfidooxidans and Metallosphaera sedula) use atmospheric carbon dioxide (CO₂) as a carbon source and inorganic compounds such as iron (Fe2+), elemental sulfur (S°) and/or reduced sulfur compounds as an energy source. In addition, most of them display tolerance to high concentrations of toxic heavy metals, making them an ideal group for processing various polymetallic sources. It should be however noted that autotrophs cannot grow directly as a result of oxidation/ dissolution of the WEEE matrix - they need an additional energy source for autotrophic growth, which may be the addition of pyrite to the leaching mixture. Microbial oxidation of sulfide minerals will result in the production of acidity and iron ions, which in turn can extract metals from WEEE, leaving the non-metallic fraction intact (Isildar et al., 2019).

Biological leaching of metals from WEEE is synergistically supported by both biogenic sulfuric acid and iron ions and relies on acidolysis and redoxolysis mechanisms.

In the presence of iron, considered as a potential energy source for microorganisms, biooxidation of Fe(II) ions to Fe(III) occurs, which is responsible for oxidation of insoluble form of Cu_0 to the soluble form of Cu^{2+} according to the following equations (Awashti et al., 2019):



Fig. 2. Conventional autotrophic bioleaching of primary ores and heterotrophic and autotrophic bioleaching of secondary raw materials (Isildar et al., 2019) Rys. 2. Konwencjonalne autotroficzne bioługowanie rud oraz heterotroficzne i autotroficzne bioługowanie surowców wtórnych (Isildar et al., 2019)







Fig. 4. Enzymatic pathways used by sulfide-oxidizing microorganisms (Poser et al., 2014) Rys. 4. Szlaki enzymatyczne wykorzystywane przez bakterie siarkowe (Poser et al., 2014)

 $\begin{aligned} &2Fe^{2+} + 1/2 O_2 + 2H^+ \ Fe-oxidasiers \rightarrow 2Fe^{3+} + H_2O \ (Microbial) \\ &2Fe^{3+} + Cu^0 \rightarrow 2 \ Fe^{2+} + Cu^{2+} \ \Delta G^\circ = 82,9 \ kJ/mol \ (Chemical) \end{aligned}$

The biooxidation of Fe(II) to Fe(III) is an acid consuming reaction, so the addition of acid during the bioleaching process is required to control the reaction. It also prevents the unwanted precipitation of iron. The bioleaching rate depends primarily on the initial pH, the initial Fe²⁺ ion concentration, and the rate of oxidation of Fe(II) ions to Fe(III). The concentration of biogenic Fe³⁺ is directly correlated with the leaching rate of the leached metal as a function of time and the total extraction efficiency (Bas et al., 2013).

Copper extraction can also occur in the absence of iron by using elemental or reduced sulfur as an energy source (Fig. 3 and 4). In this process, carried out under aerobic conditions, the protons formed are responsible for the solubilization of copper with zero valence according to the equation (Awashti et al., 2019):

 S^{0} + 1,5 O_{2} + $H_{2}O$ → SO_{4}^{2-} + 2 H^{+} (Microbial) 4 H^{+} + 2 Cu^{0} + O_{2} → 2 $H_{2}O$ + 2 Cu^{2+} (Chemical)

Solubilization of metals such as Al, Ni and Zn depends on mechanisms consistent with their thermodynamic reactions given below (Awashti et al., 2019):

$$\begin{split} 3Fe^{3+} + Al^{0} & \rightarrow 3Fe^{2+} + Al^{3+} \Delta G^{\circ} = 1085, 2, 9kJ/mol\\ 2Fe^{3+} + Ni^{0} & \rightarrow 2Fe^{2+} + Ni^{2+} \Delta G^{\circ} = 196, 6kJ/mol\\ 2Fe^{3+} + Zn^{0} & \rightarrow 2Fe^{2+} + Zn^{2+} \Delta G^{\circ} = 295, 4kJ/mol \end{split}$$

The efficiency of the metal bioleaching process from WP-CBs can be increased by externally supplying iron(II) and sulfur to the culture medium especially for low iron content wastes (Lambert et al., 2015; Latorre et al., 2016; Ilyas et al. 2013). This can be explained by the partial compensation of acid consumption through S0 oxidation, which creates more suitable conditions for the bacteria.

Heterotrophic bioleaching of WEEE

Bacteria (Pseudomonas strains such as P. aeruginosa, P. fluorescens and P. putida and Chromobacterium violaceum), archaeons and fungi(Aspergillus niger, Penicillium simplicissimum) are involved in the heterotrophic bioleaching of metals. Heterotrophic microorganisms can tolerate high pH as well as metals complexed in the solution. Furthermore, compared to acidophiles, heterotrophs tolerate a wider pH range and can be used to treat moderately alkaline wastes. Heterotrophic bacteria and fungi contribute to bioleaching either by biosynthesis of organic acids (acetic, lactic, formic, oxalic, citric, succinic and gluconic acids) or production of cyanides which solubilize metals. Cyanogenic bioleaching targets precious metals and platinum group metals (PGMs), i.e. Au, Ag, Pt, Pd, Rh, and Ru, which often cannot be leached with mineral acids (Isildar et al., 2019).

Materials and methods

Pretreatment of WPCBs

Printed circuit boards were separated from mobile phones manually and then crushed in a hammer mill. Three-stage shredding was performed. The first stage involved shredding using a 15mm sieve. The shredded material was classified on a 1mm sieve. Sieving resulted in obtaining a final product with a grain size of 0-1mm and retained with a grain size >1mm, which was put back to the mill. Before the second stage, the sieve was changed to a 5 mm one. The product was sieved, and the results were the same as in the previous stage: grain size 0-1mm. Grains larger than 1mm were put back to the mill. In the last stage, a 1mm sieve was used. Grain size was classified as 0-1mm. Shredding process using hammer mill made it possible to separate the grain size classes, which were subjected to further investigation. The process diagram is shown in Figure 5. During shredding, dust collectors collected dust, which, due to its low weight, constituted a ready product for examination using microorganisms. Shredded material with grain size >1mm was directed to a magnetic separator, where a magnetic and non-magnetic material were detached, which, when combined with the dust collected during the shredding process, was a source for further biological research. Next, in order to ensure sterility, the feed was cleansed using deionised water and placed in the dryer at a temperature of 80°C for 24h.

Chemical analysis

The WPCBs sample was dissolved using aqua regia and then the obtained solution was filtered and analysed for metal content using the Philips PU-9100x atomic absorption spectrophotometer. Obtained results are presented in Table 1.

To analyze the metal content of the bioleaching process, 5 ml of leaching solution was centrifuged at 10 000 RPM for 15 minutes in order to separate the biomass and then filtered using syringe filters. The supernatant obtained in such a way was analysed for the average metal content using Philips PU-9100x atomic absorption spectrophotometer.

The medium's pH change was monitored using WTW InoLab[®] Multi 9310.

Microorganisms and growth condition

The microorganism used for the bioleaching process was At. ferrooxidans (DSM 9464), obtained from the DSMZ Deutsche Sammlung von Mikroorganismenn und Zellkulturen GmbH, Germany. The bacteria was initially cultured in freshly prepared DSMZ 670 medium. For activation of the culture and to achieve higher iron oxidation rate, serially five transfers were given in 9K medium which contained: 44.22g of Fe₂SO₄·7H₂O, 3g of (NH₄)₂SO₄, 0.5g of K₂HPO₄, 0.5g of Mg-SO₄·7H₂O, 0.1g of KCl, 0.01 g of Ca(NO₃), per 1L of distilled water. Ingredients of the medium except ferrous sulphate were sterilized in an autoclave at 121°C for 15 min. Ferrous sulphate was filtered sterilized using 0.22 µm membrane filter and added to the cooled sterile medium. The culture was allowed to grow till >95% of the added ferrous iron in the medium was converted to ferric iron by the organisms. In sequential transfer, 10% v/v actively growing iron-oxidizing bacteria having ~107 cells mL⁻¹ was added into a flask containing the fresh 9K medium. Finally the medium in logarithmic phase of growth with approximately 20×10^7 cells/mL as stock culture was prepared for inoculation.

Bioleaching experiments

The bioleaching experiments were carried out in one-step proces where WPCBs powder was added initially along with



Fig. 5. Diagram of processing printed circuits board of a mobile phone Rys. 5. Schemat przeróbki płytek drukowanych pochodzących z telefonów komórkowych

Tab. 1. Chemical analysis for metal content of WPCBs Tab. 1. Analiza chemiczna zawartości metali w odpadach PCBs

Metal type	Metal content (%w/w)			
Al	0,36			
Cu	14,76			
Ag	0,0012			

the culture and the culture was allowed to grow in the presence of e-waste. Bioleaching experiments were carried out in Erlenmeyer flasks of 500 ml capacity, by using a incubator shaker Lab Companion IST-3075 at 150 rpm and 30°C. 9K medium was used in all biological experiments as a leaching solution. Samples used had the volume of 200 ml. The decrease in volume due to evaporation was compensated by the addition of sterile distilled water. Effect of medium pH (1.5, 1.8, 2.0, 2.5 and 3.0); effect of pulp density (1, 5, 10% w/v) and effect of inoculum doses (10, 20, 50%) were studied.

Influence of pH on bioleaching and bacterial growth

In order to investigate the influence of pH on bacterial growth, A. ferrooxidans stock culture were inoculated into 9K medium at volume dose of 20% (v/v) with different medium pH (1.5, 1.8, 2.0, 2.5 and 3.0). The population dynamics study of the microorganisms was carried out by measuring of microbial cells concentration with McFarland densitometer DEN-1.

In order to investigate the influence of pH on bioleaching, 2 g of WPCB powder (PD 1% w/v) were placed into four 500 ml conical flasks which contained 200 ml of 9K medium. The pH of solution was adjusted to 1.5, 1.8, 2.0, 2.5 and 3.0 by adding 1N H_2SO_4 . A. ferrooxidans bacteria was injected into the solution at quantity of 20% (v/v). The variations of pH and concentrations of metals in solution were measured with time. Experiments were carried out for 14 days in duplicate and the averaged results reported.

A. ferrooxidans stock culture were inoculated into 9K medium at volume dose of 20% (v/v) with different pulp densities (PD 1, 5, 10% w/v). The solution pH was controlled at 2.0 by adding 1N H_2SO_4 . The variations of pH, the oxidation-reduction potential (ORP), and concentrations of metals in the solution were measured with time. Experiments were carried out for 14 days in duplicate and the averaged results reported.

Onfluence of inoculum doses (ID) on bioleaching

A. ferrooxidans stock culture were inoculated into 9K medium at volume doses of 10%, 20%, and 50% (v/v). Mass of waste was constant equal to 2g (PD 1% w/v). One flask was not inoculated as a sterile control test. The solution pH was controlled at 2.0 by adding 1N H_2SO_4 . The variations of pH, the oxidation-reduction potential (ORP), and concentrations of metals in the solution were measured with time. Experiments were carried out for 14 days in duplicate and the averaged results reported.

Result and discusion

No Ag was detected in any leachate.

Effect of medium pH

Figure 6 shows the effect of different pH values on bacterial growth and activity. The results show that the appropriate pH value is in the range of 1.8-2.5, and the bacterial cell concentration is highest when the pH value is 2.0. Bacterial activity is inhibited outside the range of pH values 1.8-2.5. Therefore, exceeding the upper pH limit can significantly reduce microbial activity and thus slow down the bioleaching kinetics.

Influence of pulp density (PD) on bioleaching



Fig. 6. Effect of pH on activity of bacteria Rys. 6. Wpływ pH na aktywność bakterii



Fig. 7. Influence of pH on Cu extraction by A. ferrooxidans; PD 1% w/v; ID 20% v/v Rys. 7. Wpływ pH na ekstrakcję Cu przez A. ferrooxidans; PD 1% w/v; ID 20% v/v



Fig. 8. Influence of pH on Al extraction by A. ferrooxidans; PD 1% w/v; ID 20% v/v Rys. 8. Wpływ pH na ekstrakcję Al przez A. ferrooxidans; PD 1% w/v; ID 20% v/v



Fig. 9. Effect of inoculum dose on bioleaching process of Cu solubilisation, PD 1% w/v Rys. 9. Wpływ dawki inokulum na proces bioługowania Cu, PD 1% w/v



Fig. 10. Effect of inoculum dose on bioleaching process of Al solubilisation, PD 1% w/v Rys. 10. Wpływ dawki inokulum na proces bioługowania Cu, PD 1% w/v



Fig. 11. Effect of pulp density on bioleaching process of Cu solubilisation, ID 20% v/v Rys. 11. Wpływ gęstości zawiesiny na proces bioługowania Cu, ID 20%% v/v



Fig. 12. Effect of pulp density on bioleaching process of Al solubilisation, ID 20% v/v Rys. 12. Wpływ gęstości zawiesiny na proces bioługowania Al, ID 20%% v/v

Since bacterial activity is closely dependent on pH, therefore pH correction is very important for the biological leaching of WPCBs, a phenomenon to which other researchers have also pointed out in their work (Yang et al., 2014; Willner and Fornalczyk, 2013; Garg et al., 2019). In the bioleaching process, the consumption of H⁺ ions resulting in an elevated pH can have direct and indirect causes. Direct wear is due to reaction with alkaline substances and metals in the WPCB matrix while indirect wear is due to natural and bacterial oxidation of Fe²⁺. What is also noteworthy, during the bioleaching process, a decrease in pH and a decrease in leaching agent concentration may occur due to the precipitation of jarosite according to the following equation, where A⁺ is a monovalent cation (Hubau et al., 2020):

 $A^{+} + 3Fe^{3+} + 2SO_{4}^{2-} + 6H_{2}O \rightarrow AFe_{3}(SO_{4})_{2}OH)_{6} + 6H^{+}$

Diagrams 7 and 8 show the effect of initial system pH on bioleaching of metals from WPCBs

Biological leaching of metals from WPCBs is synergistically promoted by both sulfuric acid and iron ions. In the absence of elemental or reduced sulfur, the primary mechanism for metal bioextraction is redoxolysis using biooxidation of Fe(II) ions to Fe(III) as an energy source for microorganisms. The resulting leaching agent is a strong oxidant that reacts with metals in the waste. Therefore, during bioleaching, sufficient FeSO₄ should be present in the medium just to initiate the chain of biological transformations, since, during the process, FeSO₄ is reconstituted through the chemical oxidation of solubilized metals which reduces ferric iron back to ferrous iron. The resulting iron(II) ions are reused as an energy source. As can be seen, without bacteria or iron(II) ions, the regeneration cycle cannot continue, which affects the leaching efficiency. Additionally, the iron regeneration cycle requires the presence of H+ ions, which means that the metal bioleaching efficiency is also closely related to pH. The results of the study showed a close relationship between the initial pH and the degree of metal leaching, which is related to the effect of pH on bacterial growth and metabolic activity.

Graph analysis shows that the highest metal leaching efficiency, for Cu 90.23% and Al 60.23%, was observed at an initial pH of 2.0. However, it should be noted that the results for an initial pH value of 1.8 show little difference. At pH 1.5, 1.8, 2.0, 2.5 and 3.0, the extraction rate of copper was, respectively, 72.11; 90.23; 91.68; 78.35; 65.24%, while that of aluminum was 43.18; 58.12; 60.23; 48.95; 40.67, respectively. The reduction in extraction efficiency is due to several factors. Outside the range of 1.8-2.5, it is due to disruption of microbial growth, while at pH 2.5 and 3.0, it is due to metal precipitation, low iron(III) solubility and formation of jarosite. Similar observations have also been made by other researchers (Yang et al., 2014; Khatri et al., 2018; Garg et al., 2019).

Effect of Inoculum dose

The effect of microbial dose on metal leaching rate is shown in Figures 9 and 10.

The following extraction efficiencies were obtained during 14 days of the process depending on inoculum doses of 10, 20, 50% for Cu: 64.21; 91.68; 93.12%, respectively, while for Al: 38.12; 60.23; 63.44. As can be seen, a higher dosage of bacterial cultures accelerates the metal extraction process due to an increase in the concentration of the leaching agent in the solution. It is also important to note the comparable final extraction efficiencies for inoculum doses of 20 and 50%, which means that high extraction efficiencies can be achieved with a lower initial dose of microorganisms.

Effect of pulp density

Diagrams 11 and 12 show the effect of suspension density on the metal bioleaching process.

The study showed a decrease in metal extraction with increasing pulp density. The metal extraction efficiencies for pulp density 1; 5; 10% are 91,68; 63,22; 42,11% for Cu and 60,23; 3823; 25,55% for Al, respectively. This can be explained by a number of factors. Firstly, high suspension density involves increased concentrations of metals and matrix components that can be toxic to unadapted microorganisms. On the other hand, the WPCB matrix may contain alkaline substances such as reactive metals and organic substances which may increase acid consumption by raising the pH, thus inhibiting microbial growth and promoting Fe3+ consumption in the hydrolysis reaction. The effect of pulp density on the bioleaching process has also been noted by other researchers (Yang et al., 2014; Khatri et al., 2018; Garg et al., 2019), leveling it by adapting the bacteria to increasing waste concentrations.

Conclusions

Technological innovations and increased demand for electronic devices resulted in production of more and more waste with high metal content. This means that e-waste recycling is not only beneficial for waste neutralisation but also for the recovery of metals, including precious and rare-earth metals. Traditional e-waste recycling techniques, namely pyrometallurgical and hydrometallurgical techniques, are eco-unfriendly, energy-intensive, and noneconomic. This posed a challenge of using biotechnology to process e-waste and recover metals in an economical and environmentally friendly way. Closing the consumer cycle by recovering metals from diluted and complex waste streams will become increasingly economically viable. In addition, increasingly stringent environmental regulations and restrictions will drive demand for new methods to recycle and recover metals, especially PGMs (platinum group metals) and REEs (rare earth elements) from waste streams, providing an ideal niche for biometallurgy. The advantages of microbial processes are their specific nature, energy efficiency and minimal new waste creation. Current microbial processes face challenges associated with complex waste streams, toxicity, and competing side reactions.

The research presented in the article aimed at assessing the usefulness of the biotechnological method for leaching of selected metals from e-waste. The results indicate that it is possible to mobilize metals from WPCBs using microorganisms such as Acidithiobacillus ferroxidans bacteria. For some elements, almost complete solubilization was achieved but it can be noted that in order to recover as much metal as possible, it should be an autotrophic/heterotrophic two-step process. In the first step, bacteria can be used to solubilize Cu, Al, and in the second step, heterotrophic mold fungi can be used for selective Ag removal (Hołda and Krawczykowska, 2020).

A decrease in metal bioleaching efficiency with increasing pulp density due to direct contact of bacterial cells with the waste material containing toxic fractions is definitely a bottleneck in the up-scaling process. This impact can be reduced through adaptation of microorganisms or by using a separate process in which cells grow without waste (Arshadi and Mousavi, 2014; Arshadi et al., 2021; Ilyas et al., 2013). Nonetheless, the application of biotechnological methods on an industrial scale requires further research in order to eliminate discrepancies concerning process parameters present in the literature and optimize those parameters.

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Ekstrakcja wybranych metali z odpadowych obwodów drukowanych w procesie bioługowania bakteriami

Szybki rozwój technologiczny i wzrost popytu na urządzenia elektroniczne prowadzą do powstawania coraz większej ilości odpadów o dużej zawartości metali. Na całym świecie każdego roku wytwarza się 50 milionów ton odpadów elektronicznych (WEEE). Biorąc pod uwagę zawartość metali w nich obecnych, uważa się je za urban mining i jeśli zostaną one odpowiednio przetworzone, mogą służyć jako alternatywne, wtórne źródło metali. Szczególne znaczenie mają odpadowe obwody drukowane (WPCBs) stanowiące 3-5% WEEE. Zawierają one średnio 30-40% wagowych metali, o czystości większej niż w minerałach. Mając na uwadze korzyści środowiskowe i ekonomiczne, coraz większą uwagę przywiązuje się do rozwoju procesów odzyskiwania metali i innych cennych materiałów z odpadów PCBs. Badania przedstawione w artykule miały na celu ocenę przydatności metody biotechnologicznej do ługowania wybranych metali z odpadów elektronicznych. Wyniki wskazują, że jest możliwe mobilizowanie metali z PCBs przy użyciu mikroorganizmów takich jak bakterie Acidithiobacillus ferroxidans.

Słowa kluczowe: Acidithiobacillus ferrooxidans,, bioługowanie, odpadowe obwody drukowane, WPCBs



Effective Removing of Light Impurities from an Aggregate in SEL Separator

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Abstract

The aim of the paper is a work characteristics of innovative technological circuit for production and beneficiation of minerals aggregates. Investigative programme included separation of chalcedonite aggregate with particle size range 2-4 mm, 2-8 mm and 8-16 mm, upstream separated into regular and irregular particles. Tests were conducted in a dedicated separation device of light fractions (SEL) constructed in in HTS Gliwice, within the frames of "Formator Puls" project.

Keywords: mineral aggregate, SEL separator, chalcedonite, regular grains, pilot plant

Introduction

Enrichment of mineral aggregates is aimed at increasing their qualitative characteristics so they could meet specific standards or requirements required for a specific purpose of further industrial utilization. This process important, in particular, for gravels, broken carbonate rock aggregates or other aggregates, as well as waste (e.g. from building industry), which may be of inadequate quality due to high heterogeneity in terms of strength, water absorption, porosity, content of impurities and particle shape. Enrichment process can be carried out among others by taking advantage of the differences in apparent densities between defective and normal particles as well as differences in the strengths of individual grains. These methods are usually associated with the processes of comminution, classification, beneficiation and washing. Therefore, it is sometimes assumed that extensive enrichment processes occur simultaneously, e.g. in impact crushers (dry cleaning of aggregates from clay and organic materials) (Mazela 1998), hydraulic classifiers and jigs (removal of weathered particles with lower densities or different values of settlement velocities) (Osoba 2007), as well as in mechanical and high-pressure washing devices (Saramak et al. 2020). This applies especially to gravel aggregates, especially of glacial origin, with a clay coating on individual particles, which can be removed in washing and crushing operations. The results of recent investigations also indicate the possibility of carrying out the enrichment process by utilizing such characteristics of the grained material as shape, density and buoyancy in the water medium. This approach is based on patented technologies for the production of regular and irregular aggregates (PL 233689 B1, PL 233318 B1) (Gawenda 2014, Gawenda 2015 a, b, c).

Gravity enrichment in jigs is a simple separation method using in separation of various mineral resources and waste, and at the same time it is efficient and effective in the separation of materials with a relatively large difference in density (e.g. coal from gangue). It is also a method with a relatively low negative impact on the natural environment and has a high economic efficiency, which makes it a prospective separation method (Marx et al. 1999). The enrichment process in the jig takes place as a result of the separation of the feed into fractions of different densities. It can be carried out in air, water or other liquid medium, lighter than the ingredients of the raw material. Materials with different densities are characterized by various values of settlement velocities for a given medium, in which its vertical pulsating movement of the medium flow is generated (Stępiński 1969). As a result of the separation operation, after some time a layer of material forms on the sieve, separated into fractions according to the settlement velocity of individual particles. Finally, product fractions with greater homogeneity in terms of density, and thus higher commercial value, can obtained. If the feed contains light impurities, like roots, leaves, coal, amber, they will also be in the top layer of the jig.

The accuracy of the separation process is influenced by a number of factors, like the particle size and densimetric composition of the feed, efficiency, hydrodynamic conditions, the amount of bottom water fed, design solutions (i.e. a method of collecting of heavy product), and others. The most important parameter determining the efficiency of the jig separation process is the densimetric composition of feed. When the content of the higher-density fraction is greater than the throughput of the device, some portion of such material goes to the lighter product, which worsens the separation efficiency. As a minimum particle size that can be directed to the jig should be considered the value, below which the efficiency of its enrichment by other methods will be greater (Gawenda et al. 2019; Surowiak et al. 2020, Stępiński 1969).

Materials and methods

The main purpose of presented investigative programme was evaluation of the enrichment efficiency for a chalcedonite aggregate separated in selected particle size fractions and with different operating parameters of device in an innovative technological circuit for the production of regular aggregates and for cleaning of mineral aggregates from light organic impurities, such as wood and coal. The solution is based on the invention entitled Układ urządzeń do produkcji kruszyw oraz sposób produkcji kruszyw (patent No. 233318 B1), applicable



Fig. 1. Technological circuit for aggregate production with diverse physical and mechanical characteristics according to a patent 233318 B1 Rys. 1. Układ do produkcji kruszyw o zróżnicowanych parametrach fizykomechanicznych według patentu 233318 B

in the production of regular and irregular aggregates. As a result, it was possible to produce separately four types of aggregates with any particle size range, i.e. regular (cubic) and irregular (non-cubic) aggregates of low and high density, or regular and irregular aggregates free of light contaminations.

The method of aggregate production presented in Figure 1 is aimed at crushing of a feed materials in a crusher (No. 1) and classifying into narrow particle size fractions in a screen (No. 2), and then subjecting to a further separation process in a screen equipped with slotted screens (No. 3) in order to obtain separately regular and irregular particles, by directing them to tanks no. 4 and 5. Next, in the process gravity separation (pulsating jigs, air jigs or air classification tables - no. 6 and 7), lighter particles can be separated from heavier ones. The main purpose of separation of material into narrow particle size fractions is elimination of particles with equally settling velocities prior to separation process, as such particles are of a negative impact on the separation sharpness according to density. The accuracy of the separation process in a stream of pulsating medium depends on many factors, including: the particle size and densimetric composition of the feed, amount of feed material fed to the jig, hydrodynamic conditions, i.e. the pulsation regime, the amount (speed) of the bottom water fed, machine design solutions such as the method of discharge heavy product and others.

The achieved result of separation and the degree of washing of aggregate from organic impurities depends mainly on certain operating parameters, which can be adjusted in order to achieve the most favorable effect of the process course. The basic parameter of enrichment process is the feed flow rate, that is an amount of the material mass that flows through the device in a given time period. It is also related to the unit load of the separator - the mass of material per a unit of working area, which values should be between 2 and 35 tons per square meter multiplied by hour (Mg/(m^{2*}h). An increase in value of unit load affects a decrease in the separation efficiency and an increase in probable dispersion and imperfections indices, the lowest possible value of which indicates for a more precise separation. In the evaluation of the testing programme, the influence of selected factors related to the feed properties (size, shape and type of grains), hydrodynamic parameters of the separator's operation (water flow rate, frequency and amplitude of pulsations) as well as machine design (setting the height of the heavy fraction collection threshold) on the effect of washing of the aggregate product from organic impurities, was analyzed (Surowiak et al. 2020; Marx et al. 1999; Stępiński 1969).

The testing circuit consists of the SEL (separation device for light particles enrichment) device, which is a machine that utilizes water as a working medium for cleaning the aggregate from contaminants - mainly organic (Fig. 2). The contaminated material enters a water-filled working chamber of the machine, which creates a wave motion of the water, as a result of what the contaminants are washed out and float on the surface of the water, and then are discharged through the first overflow threshold. The jump of pulsation range is from 50 mm to 140 mm and the pulsation frequency is approximately from 60 to 90 cycles per minute. The separator is equipped with 4 polyurethane screens with 2 mm slots, the total length of which is 1160 mm and the width of 150 mm, creating a working surface of the bed 0.174 m². The maximum efficiency of the device reaches 2.750 Mg per hour, and the maximum water requirement is 5.5 m³ per hour. The product collection system is equipped with two water tanks, which previously separates from the heavy fraction (aggregate) products from water on a sieve and the light



Fig. 2. Testing circuit SEL (AGH UST in Cracow) Rys. 2. Stanowisko badawcze SEL (AGH w Krakowie)



Fig. 2. Testing circuit SEL (AGH UST in Cracow) Rys. 2. Stanowisko badawcze SEL (AGH w Krakowie)

Fig. 1. Technological circuit for aggregate production with diverse physical and mechanical characteristics according to a patent 233318 B1 Rys. 1. Układ do produkcji kruszyw o zróżnicowanych parametrach fizykomechanicznych według patentu 233318 B

Parameter	Unit	Value
Water flow rate, Q	[dm³/s]	1.3, 1.8, 2.1
Pulsation	[1/min]	60, 70, 80, 90
Jump of bellows	[mm]	50, 80
Height of the light product threshold	[mm]	150
Height of the heavy product threshold	[mm]	135, 165, 180
Content of impurities in products	[%]	0.01 - 0.89 (1,36)

fraction (organic pollutants) on the bag filter, and the water is collected in the tanks and then pumped to the main supply tanks. In this way, the flow of water through the machine is a closed system, which significantly reduces water consumption and eliminates its leakage outside the system.

The chalcedonite aggregate, previously crushed in a jaw crusher operating in a closed circuit, constituted the material for all tests. Following narrow particle size fractions were distinguished from the material: 2.0-4.0; 4.0-6.3; 6.3-8.0; 8.0-10.0; 10.0-12.0; 12.0-14.0; 14.0-16.0 mm, which were then separated into regular and irregular particles by means of appropriately selected slotted sieves, according to the procedure described in the literature (Gawenda, Lubaczewska 2019; Gawenda 2015a and b). In this way, the following samples were selected for testing programme:

Sample 1.1: 2 - 4 mm, 100% regular particles Sample 1.2: 2 – 4 mm, 100% irregular particles Sample 1.3: 2 – 4 mm, 50% regular particles Sample 2.1: 2 – 8 mm, 100% regular particles Sample 2.2: 2 – 8 mm, 100% irregular particles Sample 2.3: 2 – 8 mm, 50% regular particles Sample 3.1: 8 – 16 mm, 100% irregular particles Sample 3.2: 8 – 16 mm, 100% irregular particles

In further analyses samples with regular particles will be denoted generally as samples x.1, samples with irregular parti-

cles as samples x.2, and samples with 50% of regular particles as samples x.3. Analogous denotation will be used for categorization of samples according to size in general: samples 1.x for 2-4 mm, samples 2.x for 2-8 mm and samples 3.x for 8-16 mm.

Prior the tests, the material was deliberately contaminated with a light fraction in the form of wood roots and carbon particles in the amount of 2%. The list of all changeable parameters with individual values was presented in Table 1. There was accepted a constant height of the light fraction threshold (150 mm) and samples for analyses have been collecting for 10 seconds after the separator's operating conditions had stabilized. The experiment was carried out on the basis of the factorial experiment methodology for four variables, each had from 2 to 4 levels of variation.

Results and discussion

Effects of size and shape of particles on the washing process efficiency

Figure 4 shows the results of relationships between impurities content in the heavier (lower) product of separation and particle size distribution separately for samples x.1, samples x.2 and samples x.3. These relationships show that chalcedonite products with regular particles and particles size 2.0-8.0 mm contained more impurities (0.3%), comparing samples 1.x and samples 3.x. for Q = 1.8 and Q = 2.1 dm³/s (Figs. 4a, 4b). Samples 1.x were characterized by more favorable results, impurities constituted approx. 0.05% for both values of Q (Fig. 4c,





4d). For the sample 3.2. higher impurities were observed in the product, approx. 0.35% for Q = 2.1 dm³/s and 0.13% for Q = 1.8 dm³/s. For the sample 1.x. the content of impurities was very low – below 0.03% for all cases. In sample 3.x. the proportion of impurities in the heavy product was similarly low, while for the 60 cycles per minute and the Q = 1.8 dm³/s was higher than 0.09% (Figs. 4e, 4f).

Effect of flow rate of water and threshold value on the washing process efficiency

Figures 5-7 present the results effect of the flow rate of water to the separator on the content of impurities in the final product, for the height of the heavy product collection threshold, respectively 13.5 and 16.5 mm. For regular particles in particle size 8-16 mm (sample 3.1.), the highest values of impurities were observed for the maximum water flow (2.1 dm³/s) and the threshold height 13.5 cm (Fig. 5). Irregular particles, in

turn, were better washed for the higher value of threshold (i.e. 16.5 cm) for both settings of the water flow rate. The impurities contents in these products were below 0.15% for all pulsation ranges (Fig. 6) and even in some cases below 0.05%. For samples 3.2. and 3.3. it was more advantageous to operate with a higher threshold value (16.5 cm), however, an increase of the flow rate water from 1.8 to 2.1 dm³/s did not affect significantly the content of impurities in products.

Effect of jump and pulsation frequency on the washing process efficiency

Figures 8-10 show the effect of the pulsation frequency on impurities content in products for the samples 1.x., depending on the water flow rate Q. The height of heavy product threshold was 18 cm, and the jump 5 cm. It was easy to notice that all samples were washed very well in all ranges of pulsation frequency and water flow rate. Only for the sample 1.2. at pulsa-



Fig. 5. Effect of water flow rate Q on quality of products - sample 3.1

Rys. 5. Wpływ natężenia przepływu wody do separatora na ilość zanieczyszczeń w kruszywie - próbka 3.1



Fig. 6. Effect of water flow rate Q on quality of products - sample 3.2

Rys. 6. Wpływ natężenia przepływu wody do separatora na ilość zanieczyszczeń w kruszywie - próbka 3.2



Fig. 7. Effect of water flow rate Q on quality of products - sample 3.3

Rys. 7. Wpływ natężenia przepływu wody do separatora na ilość zanieczyszczeń w kruszywie – próbka 3.3



Fig. 8. Results for sample 1.1., jump = 5 cm, threshold = 18 cm Rys. 8. Wyniki dla próbki 1.1., skok 5 cm, próg 18 cm

tion frequency 60 and 70 cycles per minute and the maximum water flow, the content of impurities was higher by over 0.5%. In the case of minimal water flow (i.e. 1.3 dm³/s), the content of impurities was very low, and equaled even zero for sample 1.2. Therefore, it can be concluded that for the fine particles (2-4 mm) enriched in the SEL separator, it is advantageous to prepare regular and irregular particles separately, because it allows for very thorough cleaning with reduced water consumption.

Figures 11-13 show effects of enrichment for coarser particles in the wider particle size range, which can be considered as favorable. For the pulsation of 60 cycles per minute, the content of impurities in the product exceeded 0.5% only in one case (Fig. 13). For coarse particles, it is more advantageous to run the process with a higher height of heavy product collection threshold, and for that case the water flow rate can be reduced to $1.8 \text{ dm}^3/\text{s}$.

Summary and conclusions

The results of investigations show that application of enrichment operations in jigs separately for the feed material containing regular and irregular particles makes it possible to obtain the product aggregate with improved qualitative characteristics and a homogeneous particle shape. A detailed analysis of results shows that thanks to appropriate preparation of feed ma-







Fig. 10. Results for sample 1.3., jump = 5 cm. Rys. 10. Wyniki dla próbki 1.3., skok 5 cm







Fig. 12. Results for sample 3.2., jump = 8 cm Rys. 12. Wyniki dla próbki 3.2., skok 8 cm



Fig. 13. Results for sample 3.3., jump = 8 cm Rys. 13. Wyniki dla próbki 3.3., skok 8 cm

terial prior the enrichment, i.e. classification into narrow particle size fractions and into regular and irregular particles, and by controlling the separation process in SEL through specific adjustments of selected parameters (jump, pulsation frequency, water flow rate), it is possible to obtain high purity products. It can be also achieved a reduction of impurities content from 2% (for feed material) to even 0% (for specific products).

By examining the impact of the particles size and shape on effectiveness of enrichment process the accuracy of cleaning the aggregate from impurities, it can be concluded that it is more advantageous to separate particles in terms of shape, as well as classification into fractions of a narrower particle size range. A higher setting of the threshold gives better results in terms of removing of organic impurities from samples with wider particle size fractions, i.e. 2.0-16.0 mm. On the other hand, in the case of a narrower fraction (2.0-8.0 mm) and finer particles, it is more advantageous to carry out the process at low water flow rate Q and with a low height of the product collection threshold. Here, in addition to a very low impurities content in products, an advantage is also the limitation of the water flow rate through the circuit. The results of conducted tests for coarse particles within particle size fraction 8-16 mm showed that the value of pulsation jump in separating device should be set at 8 cm. For fine particles, finer than 8 mm, good enrichment results were achieved for lower pulsation jump (5 cm). Even better results in terms of purity of products and water consumption were achieved in separation of the material in terms of shape.

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Efektywne usuwanie frakcji lekkiej z kruszywa w separatorze SEL

Celem artykułu jest charakterystyka pracy innowacyjnego układu technologicznego służącego do produkcji i uszlachetniania kruszyw mineralnych. W ramach badań przetestowano proces uszlachetniania kruszywa chalcedonitowego o uziarnieniu 2-4 mm, 2-8 mm i 8-16 mm rozdzielonego na frakcje z ziarnami foremnymi i nieforemnymi w specjalnie skonstruowanym i zabudowanym w laboratorium separatorze frakcji lekkiej – SEL zbudowanym przez HTS Gliwice w ramach projektu Formator Plus.

Słowa kluczowe: kruszywo mineralne, separator SEL, chalcedonit, ziarna foremne, instalacja pilotażowa



Adsorption of the Petrochemical Pollutants Released at the Small Vehicle-Service Facilities on the Coal Refinery Sludge/Pyrocarbon Compositions

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Abstract

It has been proven that the use of coal-like adsorbents with the mosaic and hydrophobic surface structure is efficient in cleaning the wastewater from a wide range of pollutants under the condition of their uncontrolled release from various small enterprises. This range includes such environmentally dangerous agents as petrochemicals and other pollutants formed at car filling, carwash stations or other similar facilities. Technical pyrocarbon and the coal refinery sludges are readily available waste materials with high porosity, which exhibit some adsorption activity and can be utilized in water/wastewater treatment solutions. Then the adsorbents can be either disposed of at the landfill areas or incinerated as components of some secondary fuels. The highest adsorption performance is achieved for the sorbent mixture of the refinery sludges and technical pyrocarbon with the ratio of the components 4:1. If the wastewater is flowing through this composition, the degree of petrochemicals removal reaches 75-80% for the mixture sludge/ technical pyrocarbon, while the pure pyrocarbon ensures the removal degree of 15-20% only. Though adsorption efficiency under stationary conditions (keeping the adsorbent and the wastewater in contact inside some decontamination pond/vessel for at least 24 h) is higher, this option is hard-to-realize for a small car service/wash station. As an alternative, comparatively small wastewater cleaning cartridges filled with the 4:1 mixture of coal sludge and technical pyrocarbon can be recommended for preliminary decontamination of the wastewater formed at such enterprises before their discharge to the local municipal sewerage lines.

Keywords: coal refinery waste, pyrocarbon, adsorption efficiency, petrochemicals, pollution, wastewater treatment technologies

Introduction

Environmental pollution with oil and petrochemical products is one of the most dangerous consequences of human-induced activity. Petrochemical products affect human and animal bodies, water plants, physical, chemical and biological condition of the water objects. The maximum possible concentration (MPC) of petrochemical products in the household and drinking waters in Ukraine is 0.3 mg/L, and MPC of petrochemical products in the fishery utilization water is limited by 0.05 mg/L [1, 2]. These limitations are quite strict, and it is required to apply various water/wastewater treatment technologies to remove or decontaminate the petrochemical pollutions of water and bring its quality parameters within these limits. This issue is especially acute since many carwash, filling and service stations usually discharge their wastewater into the local municipal sewerage without any special treatment. As a rule, this wastewater is severely contaminated with various petrochemicals coming from the vehicle oils, grease, corrosion protection materials, spills of fuel and other liquids, and other similar sources [3-5].

An ordinary carwash produces an average of $0.7 \div 1.2 \text{ m}^3$ of wastewater a day. Such wastewater contains about $800 \div 3000 \text{ mg/L}$ of suspended substances and $500 \div 900 \text{ mg/L}$ of petrochemical products [3, 4]. The car filling stations discharge a lesser amount of wastewaters but with much higher pollution [6].

A wide variety of methods and technologies or their combinations is applied for reuse, reclamation and cleaning of these wastewaters: regular filtration, chemical, photo- or electro-oxidation, various kinds of adsorption, extraction, biotreatment, and others [7, 8]. Adsorption is one of the highly effective wastewater cleaning methods. Previously it has been established that graphite or activated charcoal is a more effective adsorbent for some petrochemicals than inorganic clays or silica gel [9, 10]. It has also been found that the process of toluene adsorption on graphite or activated charcoal materials occurs according to the mixed kinetic/diffusion control mechanism [11]. However, the efficiency of the adsorption of various petrochemical compounds can vary within significant limits [12]. Carbon nanotubes have shown even better efficiency in petrochemicals adsorption [13], but this material is still quite expensive while various pyrocarbons are abundant and readily available at a comparatively low price. The same is true for the coal sludges usually collected as waste or by-product at the coal refinery plants.

From a competitive point of view, it is important to keep the treatment process easy and relatively cheap, making the introduction of such technologies feasible for small companies. Thus, mobile and replaceable wastewater treatment modules are reasonable for extraction of the relatively low amounts of wastewaters formed at the low-tonnage pollution discharging points before their release to the sewage.

Considering the physical and chemical characteristics of the oil products and following the abovementioned results of the previous investigations, it is expected that the adsorbents with the hydrophobic surface should be the most efficient for such treatment technologies.

Pyrocarbon or semi-cake is a hydrophobic material obtained as the solid residue in the pyrolysis of various non-compostable polymer and rubber wastes. It is cheap,



Fig. 1. Dependence of the wastewater absorbance on the adsorbent concentration in the case of 'static' (see explanations in the text) treatment conditions:
 (•) – pyrocarbon;
 (•) – coal sludge;
 (Δ) 4:1 mixture of the sludge and pyrocarbon. Vertical bars show the relative experimental ranges for each experimental series.

Rys. 1. Zależność absorbancji ścieków od stężenia adsorbentu w przypadku "statycznych" (zob. wyjaśnienia w tekście) warunków oczyszczania: (•) karbonizat; (•) - muł węglowy; (Δ) 4:1 mieszanina szlamu i karbonizat. Pionowe słupki pokazują względne zakresy eksperymentalne dla każdej serii eksperymentalnej.

highly porous and can be used in numerous technological applications as a secondary fuel or charcoal substitute.

Some admixture of the sludge (a by-product of coal refining) can also be used as a cheap component of the adsorbent composition. However, it should be clarified how this component will influence the adsorption efficiency of pyrocarbon.

In this work, a comparative efficiency of pyrocarbon, coal sludge and the pyrocarbon/sludge composition has been investigated in the adsorption of petrochemical mixtures using absorbance or the chemical oxygen demand (COD) index as a method of determination of the total concentration of petrochemicals in water.

Materials and experimental methods

Wastewater samples were collected from a conventional carwash station in Chernivtsi, Ukraine. They were taken from an accumulation tank where the untreated wastewater is collected before being discharged to the municipal sewerage.

The following materials were tested as adsorbents:

- Coal refinery sludge of the T-brand coals obtained at Kondratyevska Central Mining and Processing Enterprise, Ukraine. The material humidity is 15.0% and the ash content is 43.1%.
- Technical pyrocarbon obtained after the pyrolysis of various unsorted polymer wastes. The material humidity is <1% while the ash content is about 29.5%.
- 3. A mixture of the sludge and pyrocarbon with the mass ratio 4:1

It has been found previously [14] that this ratio of the components ensures the highest anti-sedimentation stability because highly dispersed pyrocarbon particles form the mixed contact aggregates with the sludge preventing them from being washed out. Therefore, it is expected that this composition would exhibit the highest anti-agglomeration stability, the easiest access to the entire surface of the particles and the best adsorption performance. That is why it was used as another adsorbent.

All samples of the adsorbent were ground using the ball grinder. Then the 0.5-50 μ m fractions of each adsorbent were

separated using the appropriate sieves and used in the experiments.

The following physical and chemical characteristics of the wastewater were determined: optical density (absorbance) and chemical oxygen demand (COD). These parameters are important for the understanding of the degree of water contamination with suspended particles and the chemically oxidizable compounds (mostly organic petrochemicals). Further, these parameters were used to evaluate an efficiency of the adsorbents.

An approximate COD of the samples was determined according to the simplified procedure [15]: 5 mL of the filtered sewage water were mixed with 5 mL of the 0.1 N solution of potassium dichromate in the 250 mL conical flask, and then 15 mL of the concentrated sulfuric acid were added gradually at the constant stirring. Then 50 mL of the distilled water were added, and the mixture was heated up to the boiling point and kept 2 h at this temperature. After cooling down to room temperature, the sample was titrated by the 0.1 N solution of the Mohr's salt FeSO₄*(NH₄)₂SO₄*6H₂O against the redox indicator ferroin until the distinct change in the indicator color from blue-green to reddish. Same manipulations were done simultaneously with the control probe consisting of distilled water instead of the sewage water.

COD value was calculated by the formula:

 $COD = 8^{*}(V_{0} - V) * 0.1$ /A, where V_{0} and V are the volumes of the Mohr's salt solution spent for titration of the control and test samples (mL); 0.1 – the Mohr's salt solution normality; 8 – the oxygen equivalent; A – the volume of the test sample taken for the analysis (mL).

The absorbance of the samples was determined by the photoelectric colorimeter KFK-2 by LOMO at the wavelength $\lambda = 540 \text{ nm} [5]$.

Adsorption efficiency was evaluated either under the static conditions (some amount of the adsorbent was added to the sewage water) or under the dynamic conditions (sewage water was pumped through the adsorbent bed).

When evaluating the static adsorption efficiency, some adsorbent (0.5-17 g) was added to 25 mL of the sewage water.



Fig. 2. Dependence of the wastewater COD (mgO₂/L) in the case of 'static' (see explanations in the text) treatment conditions: (•) – pyrocarbon; (•) – coal sludge; (Δ) 4:1 mixture of the sludge and pyrocarbon. Vertical bars show the relative experimental ranges for each experimental series.
Rys. 2. Zależność ChZT ścieków (mgO₂/L) w przypadku "statycznych" (patrz wyjaśnienia w tekście) warunków oczyszczania: (•) - karbonizat; (•) - muł węglowy; (Δ) 4:1 mieszanina szlamu i karbonizatu. Pionowe słupki pokazują względne zakresy eksperymentalne dla każdej serii eksperymentalnej.

The mixture was stirred and left for 24 hours, then filtered through the "Red Tape" filter paper, and the filtrate was used in the follow-up investigations. The control test with the distilled water sample was processed by the same procedure simultaneously. An amount of the added adsorbent was limited by 17 g because, according to the experimental data, a dependence of the adsorption efficiency on the adsorbent amount reached its limit value (the dependence line slope turned practically horizontal – see Fig. 1 and 2) when this amount was close to 15 g. Therefore, further addition of the adsorbent was not reasonable as it would not cause any noticeable progress in the wastewater decontamination.

When evaluating the dynamic adsorption efficiency, a porous fabric was placed in the Buchner's funnel (diameter 8 cm), a 25 g sample of the adsorbent was poured into the funnel and covered with another porous fabric. The funnel was installed in the Bunsen's flask, and then the sewage water was vacuum filtered through the funnel. The constant vacuum of 0.3 atm produced by the electric vacuum pump was applied in all the experiments throughout this series.

Results and Discussion

Obviously, the more adsorbent added, the more petrochemicals can be captured and removed from the system. However, when present in the water-based system, the petrochemicals form two phases – the surface film and the bulk phase.

Coal sludge is a material that consists of two phases: the hydrophobic (the coal-like components) and the hydrophilic (mineral components) ones. That is why its wettability is comparatively high and its adsorption efficiency reaches 80% (see the dependence of the system's absorbance in Fig. 1). On the other hand, the sludge particles do not float and, therefore, if not stirred, the adsorption process occurs mostly in the bulk and does not involve the surface film.

Pyrocarbon, in contrary, is mostly hydrophobic material that is not wettable and, consequently, in case of using this adsorbent, the process involves mostly the surface film leaving the bulk pollutants intact. As a result its efficiency is lower and reaches only 15-20% (see Fig. 1).

The 4:1 mixture of the above components ensures the most efficient removal of the petrochemicals both from the

surface layer and the bulk of the system and the overall decontamination ratio, in this case, reaches 85-90% (see Fig. 1). As seen from Fig. 1, the wastewater absorbance decreases from 1.05 to 0.15 after adsorption by the 4:1 adsorbents mixture. This change corresponds to an 85% decrease in the concentration of the optically active water pollutants.

Similar tendencies have been registered for the wastewater COD after its treatment with the three types of the adsorbents (see Fig. 2).

It should be understood that practical realization of this static water treatment scheme would require a specialized water treatment/decontamination pond that can hardly be put in practice in the case of a small car-washing station or any similar enterprise.

That is why the efficiency of a more feasible dynamic water treatment approach has been investigated at the next stage of this work. According to this approach, the contaminated water or wastewater must be pumped through a relatively small cartridge filled with the adsorbent. This approach is less material, energy, and resources demanding and seems quite feasible even at a small-size car service or washing station.

The 4:1 mixture ensures the best adsorption efficiency, followed by the sludge and then pyrocarbon (see Table 1). In the latter case, the adsorption takes place within the surface layer only. Usually, the petrochemicals stay mostly on the surface and, taking into account this fact, the "surface" efficiency of pyrocarbon seems unexpectedly low. However, it should be understood that the detergents are used in the regular operation of car wash stations, and therefore there are considerable amounts of detergents present in the wastewater. They promote better emulsification of pyrocarbons with water and increase the bulk concentration of this pollutant, which is not affected by the purification with pyrocarbon. That is why the performance of this adsorbent is noticeably worse than for the other two materials.

At the next stage, the efficiency of the dynamic purification of wastewater was investigated. 1, 2 or 3 liters of wastewater were used in this experiment (see further details related to the experimental procedure above, in "Materials and Experimental Methods"). The initial COD of the wastewater samples was 3000 mg O_2/L , and the absorbance was 1.05. The same

Adcorbont	Absorbance			COD, mg O ₂ /L			
Ausorbent	1 L	2 L	3 L	1 L	2 L	3 L	
Sludge	0.32	0.32	0.33	650	650	680	
Pyrocarbon	0.65	0.67	0.7	1900	1950	1950	
Sorbents mixture	0.2	0,21	0,21	420	440	450	

Tab. 1. Some water quality parameters of the wastewater samples after passing through the adsorbent layer Tab. 1. Wybrane parametry próbek ścieków po przejściu przez warstwę adsornbenta

parameters are given in Table 1 for the samples after they were treated with different sorbents.

It can be seen that the sorbents mixture remains the most efficient adsorbent, followed by the sludge and then – pyrocarbon. The dynamic adsorption efficiencies with the use of coal slacks and sorbent mixture are close to those in the static conditions (maximum efficiency also reaches 75-80 %). Some insignificant decrease in the dynamic efficiency is caused by a lesser contacting time between the contaminated water and the adsorbent resulting in incomplete adsorption of the petrochemicals.

However, in the dynamic treatment, the pyrocarbon efficiency is noticeably higher than that for the static conditions. In our opinion, this is caused by the fact that pyrocarbon is fixed between two porous layers having the wastewater flux flowing through this bed. Under such conditions, pyrocarbon cannot float, and the entire water phase contacts with the sorbent surface, improving the degree of water purification as compared with that in the static conditions when pyrocarbon interacts within the surface layer only. Nevertheless, pyrocarbon, an extremely hydrophobic material, remains the worst adsorbent among the materials involved in this investigation.

It should also be emphasized that all adsorbents mentioned above can easily be utilized after their use as adsorbents for the petrochemical pollutanrs. There are many options for reuse of such materials as the components of secondary fuel [16]. In this case, they can be incinerated in specially designed water heaters, and the captured petrochemical would only increase their heat productivity.

Conclusion

Coal sludges, technical; pyrocarbon and the 4:1 mixture of these components can be used as efficient adsorbents in the wastewater treatment solutions for small car wash, service and filling stations. A reliable technology involving simple cartridges loaded with the 4:1 components mixture can ensure the purification of the technological wastewaters before the discharge to a local sewerage system. The petrochemicals extraction efficiency reaches 75-80 %, although an issue of the effective operation limits still has to be investigated for different cartridge designs and adsorbent loads.

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Adsorpcja zanieczyszczeń petrochemicznych uwalnianych w małych obiektach serwisowych pojazdów na kompozycje osadu weglowego/piroweglowego

Wykazano, że zastosowanie adsorbentów węglopochodnych o mozaikowej, hydrofobowej strukturze powierzchni skutecznie oczyszcza ścieki z szerokiej gamy zanieczyszczeń. Adsorbowane są niebezpieczne dla środowiska substancje takie jak produkty petrochemiczne i inne zanieczyszczenia powstające na stacjach paliw, myjniach samochodowych lub innych podobnych obiek-tach. Techniczny karbonizat węglowy i szlamy z rafinerii węgla są łatwo dostępnymi materiałami odpadowymi o wysokiej porowatości, które wykazują pewną aktywność adsorpcyjną i mogą być wykorzystywane do oczyszczania wody/ścieków. Następnie adsorbenty mogą być albo składowane na składowiskach odpadów, albo spalane jako składniki niektórych paliw wtórnych. Najwyższą wydajność adsorpcji uzyskuje się dla mieszaniny sorbentów z osadów rafineryjnych i karbonizatu technicznego o stosunku składników 4:1. Jeżeli ścieki przepływają przez tę kompozycję, stopień usunięcia petrochemikaliów osiąga 75-80% dla mieszaniny osad/karbonizat techniczny, podczas gdy czysty karbonizat zapewnia stopień usunięcia tylko 15-20%. Chociaż wydajność adsorpcji w warunkach stacjonarnych (utrzymywanie adsorbentu i ścieków w kontakcie w naczyniu dekontaminacyjnym przez co najmniej 24 godziny) jest wyższa, ta opcja jest trudna do zrealizowania w przypadku małych stacji obsługi/myjni samochodowych. Jako alternatywę można polecić stosunkowo niewielkie wkłady do oczyszczania ścieków wypełnione mieszaniną mułu węglowego 4:1 i technicznego karbonizatu do wstępnego odkażania powstających w tego typu przedsiębiorstwach ścieków przed ich odprowadzeniem do lokalnych miejskich sieci kanalizacyjnych.

Słowa kluczowe: odpady z rafinerii węgla, karbonizat, efektywność adsorpcji, petrochemia, zanieczyszczenia, technologie oczyszczania ścieków



Leachability of Heavy Metals from Autoclaved Fly Ash-Lime Building Bricks

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Abstract

The fly ash as a byproduct of coal-fired power plants constitutes vital ecological problems. In Turkey, approximately 15 million tons of ashes are generated via the combustion of 40 million tons of lignite yearly. Worldwide, a number of investigation and applications were undertaken to utilize fly ash in order to overcome the environmental problems. One of the application area of fly ashes is the production of building bricks. Characterization of fly ash samples from Seyitomer and Yatagan coal-firing power plants were conducted in this study. TCLP 1311, ASTM3987-85 and EN 12457-2 leaching tests on the cylindrical fly ash/lime brick (FA/LB) samples which were produced from Seyitömer and Yatagan thermal power plant fly ash-lime mixtures were performed to determine the leachability of some chosen trace elements. The results show that the release of all trace elements was lower than the hazardous material limit values of waste acceptance. Thus, non- fired fly ash bricks are an advantageous way to solving environmental effect of disposal of fly ashes.

Keywords: coal fly ash, fly ash/lime brick, leaching, trace elements

1. Introduction

According to the statistical data, Turkey is in the first ten ranking major countries of the world with coal and lignite production and consumption (http://www.enerji.gov.tr/en-US/ Pages/Coal). The hard coal and lignite reserves of Turkey are 1.3 billion tonnes and 13.9 billion tonnes respectively. Approximately 68% of the total lignite coal reserves in our country are low calorie and 23.5% of them are 2000-3000 kcal/kg (http:// www.enerji.gov.tr/en-US/Pages/Coal).

Turkey's primary energy production totaled 41.8 Mtoe in 2016, of which domestic coal provided 52.7%. Most of the lignite coal is used in energy production. Energy demand of Turkey has increased twofold over the last two decades, and this trend seems to continue in the future with an average increase of 4% per year. In the first half of 2018, 33% of Turkey's electricity production of 53,9TWh was generated in coal-fired thermal power plants (https://euracoal.eu/info/country-profiles/ turkey).

In 2017, power plants created about 10 million tons of residual product. The amount of fly ash ponded near the power plants has reached already 150 million tonnes (Akar,2001; Akar et al, 2010). Therefore, fly ash (FA) destruction, poses a major problem in Turkey. Fly ash is generally classified as hazardous waste because it is contaminated with a small amount of contaminants; including heavy metals. The assessment of the risk arising from FA is of particular importance during its utilization (Liu et al, 2009; Kosson et al., 2000; Ural, 2005; Carlson and Andriano, 2005; ASTMC 204-11, 2005)

Most of the FA derived buildings materials such as concrete, cellular aerated concrete, foam concrete, building bricks, FA stabilized soil and many others will be exposed to rain. Therefore, it is significant to determine the leachability of pollutants such as toxic metals from FA derived materials. Laboratory leaching tests are usually conducted to assess the long-term effect of possibly hazardous constituents on soil, surface and groundwater. They define leach potential of pollutants during the use or discarded mate-rials (Cetin et al., 2012; Cinquepalmi et al., 2008). Unfortunately, there is no standard or accepted method for testing the effect of rain on pollutant leachate from FA and FA derived building materials. Therefore, researchers developed different leaching tests to describe and evaluate the pollutants that could be released from FA. There is a variety of leaching tests with different varia-bles such as solid to liquid ratio (S/L), chemical reagents, temperature and contact time (Terzic et al., 2012; Johnson et al., 1999). The procedures simulate leaching behavior of coal ash and the results obtained are generally not directly comparable; However, they can show the general mobility of toxic elements in fly ash (Cappuyns and Swennen, 2008; Vitkoca et al., 2009).

The number of the research on description and industrial application of fly ash have enlarged significantly over the years. Consequently, nowadays fly ash can useable in many different sectors (Kosson, 2000, Lea, 1980; Kouskouzas et al., 2010; Lee et al., 2017). Limited amount of FA, primarily for cement and concrete production, is being employed in Turkey. Using FA as a main raw material to make light-weight building bricks is recently investigated with encouraging results (Prinya and Ubolluk, 2018; Çiçek and Cincin, 2015). Re-cently, tests have been done on determining the leachability of heavy metals from FA and FA derived materials (Tanrıverdi, 2006; Zermeno et al., 2013; Hjmelmar et al., 2007; Lidelöw and Lagerkvist 2007; Ferreira et al., 2003)).

The objective behind conducting this research work was to study chemical, mineralogical and morphological characteristics of fly ashes and evaluate the extent to which pollutants leach from the autoclaved fly ash/lime bricks (FA/LB). For this purpose, TCLP-1311 method (US-EPA 1992), ASTM D3987-85 (ASTM 2004) (ASTM, 2004) and one stage water batch test

			•	
	Mean size (µm)	Specific gravity (g/cm ³)	Specific surface area (m²/g)	Natural pH
SOFA	156	2.18	15.7	11.26
YFA	108	2.45	3.2	12.59

Tab. 1 Some physical properties of SOFA and YFA Tab. 1. Wybrane właściwości popiołów lotnych SOFA i YFA

Tab. 2. Chemical composition and trace element concentrations of - 0.212 mm SOFA and YFA
Tab. 2. Skład chemiczny i zawartości pierwiastków śladowych we frakcji -0,212 mm popiołów SOFA i YFA

Major elements (%)	SOFA [33]	YFA	Trace elements (mg/kg)	SOFA	YFA
SiO ₂	56.67	52.97	As	95	48
Al ₂ O ₃	17.33	18.19	Ва	242	233
CaO	5.34	14.97	Cd	2.7	2.3
MgO	4.1	2.25	Со	5.1	7.8
Na ₂ O	0.81	0.75	Cr(total)	264	102
K ₂ O	2.58	2.40	Cu	101	71
MnO	0.1	0.04	Мо	1.1	1.6
Fe ₂ O ₃	9.99	6.61	Pb	0.9	2.9
TiO ₂	0.14	0.25	Sr	159	197
SO ₃	1.15	0.82	Zn	150	98
Free CaO	0.32	2.18	Ni	772	84
LOI	1.75	0.71	Ag	<0.2	2.1



Fig. 1. Size distribution plots of SOFA (a), YFA fly ash (b) Rys.1. Skład ziarnowy popiołu SOFA(a) i YFA(b)

EN-12457-2 (CEN 2002) (CEN, 2002) were applied on the FA/LB samples.

2. Materials and Method

2.1 Fly ash and fly ash/lime brick samples and characterization

Fly ash samples were taken from two different lignite fired power plants from the western Turkey. The Seyitomer (SO) and Yatagan (Y) power plants use low quality lignite and generate about 0.9 million and 1.1 million ton of fly ash, respectively. Seyitomer fly ash (SOFA) and Yatagan fly ash (YFA) can be categorized as F-class low-lime FA according to ASTM C 618 standard (ASTM 2000). Using a fly ash and quenched lime, a cylindrical fly ash-lime brick (FA/LB) of 45 mm diameter and 100 mm length was made at 12-bar pressure with laboratory size steam autoclave as described by Cicek & Cincin (2015).

In this work, particle size analysis of the SOFA and YFA were determined using Horiba brand LA 950 V2 laser diffraction particle size analyzer. The specific surface area of both fly ashes were determined in accordance with ASTM C 204-11 (ASTM, 2005). The chemical analysis results of the fly ash samples was conducted using Analytic Jena NovaA 300 AAS. Agilent Technologies 7700 series ICP-MS was used to determine the trace element concentrations. Physical and chemical properties of the SOFA and YFA are tabulated in Table 1. The particle size distributions are shown in Figure 1.

The mineralogical compositions were recognized using Rigaku Miniflex-2 X-ray diffractometer (XRD) at Cu–K α ra-



Fig. 2a. XRD analysis results of the FAs and FA/LBs (A= Anortite, An=anhydrite, Q=quartz, L=lime, H= hematite, K=Katoite, T=Tobermorite, CSH=Calcium Silicate Hy-drate, M=Mullite, Mag=Magnetite, G=Gehlenite, Mf=Magnosioferrite)

Rys. 2a. Wyniki analizy XRD FA i FA / LB (A = anortyt, An = anhydryt, Q = kwarc, L = wapno, H = hematyt, K = katoit, T = tobermoryt, CSH = hydrat krzemianu wapnia, M = mulit, Mag = magnetyt, G = gehlenit, Mf = magnosioferryt).



Fig. 2b. XRD analysis results of the FAs and FA/LBs (A= Anortite, An=anhydrite, Q=quartz, L=lime, H= hematite, K=Katoite, T=Tobermorite, CSH=Calcium Silicate Hy-drate, M=Mullite, Mag=Magnetite, G=Gehlenite, Mf=Magnosioferrite)

Rys. 2b. Wyniki analizy XRD FA i FA / LB (A = anortyt, An = anhydryt, Q = kwarc, L = wapno, H = hematyt, K = katoit, T = tobermoryt, CSH = hydrat krzemianu wapnia, M = mulit, Mag = magnetyt, G = gehlenit, Mf = magnosioferryt)

diation, 30kV, 15 mA. Morphological investigations were conducted with Jeol JXA 733 microprobe, scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS).

2.2 Batch leaching tests

Mobility of trace elements in fly ash/lime bricks was determined by using serial leaching test, TCLP-1311 method, ASTM D3987-85 and one stage water batch test (EN-12457-2). Each procedure needs the application of specific test conditions. TCLP-1311 method and ASTM D3987-85 were applied on FA/LB samples as described by Akar at al. (Akar et al., 2012). The EN 12457-2 leaching test was carried out at a ratio of L/ S=10 L/kg. A mixed samples, 40g FA/LB samples and 400 ml deionized water, was placed in 500 ml polyethylene bottles. The mixture in the bottles was then shaken for 24±0.5 h at 10 rpm in a horizontal oscillating shaker. All the mixtures were kept for 5 minutes, and then the aqueous phase separated by decantation. After the pH of the leachate was measured, it was filtered through a 0.45 mm membrane filter paper with a vacuum filtra-tion system and then acidified to pH<2 using high purity nitric acid for analysis. The leached amount of the components was matched with the leaching limit values suggest-ed by the European Council decision 2003/33/EC (C. Decision, 2003).

3. Results and Discussions

3.1 Physical/chemical and mineralogical characterization of Seyitomer and Yatagan fly ashes

Specific gravities, particle size, specific surface area and pH are the most important physical and chemical factors for determining the leaching behavior of the pollutants from fly ash (Koukouzaset al., 2011; Akar et al., 2012)]. Figure.1 depicts size distributions for SOFA and YFA. The graph shows that particle size of SOFA is below 0.800 mm and 0.212-0 mm fraction makes up 76.06% of the ash. YFA is below 0.300 mm and 0.212-0 mm fraction makes up 84.14% of the ash. SOFA has a triple modal particle size histogram (Figure. 1a), while YFA has a monomodal distribution (Figure.1b). Some physical properties of SOFA and YFA tabulated in Table 1.

Behavior of trace elements in aqueous environment is related to the natural pH value of fly ash. The pH of the slurry obtained by adding 200 ml deionized water and 10 g fly ash was measured and recorded at 1 hour intervals over a 24 hour period using a WTW brand pH/Cond. 320 portable water meter (Akar et al., 2012). Both fly ashes have the alkaline character, which can be explained by the calcium content being mainly in the form of lime and soluble metal salts, oxides and carbonates. Chemical analysis and trace element concentrations are given in Tables 2.

Mineralogical properties are another important factor for the leachability of trace ele-ments from fly ash. The XRD analyses on SOFA and YFA in comparison with SOFA/LB and YFA/ LB were performed to determine the mineralogical properties (Figure 2a, Figure 2b).

The crystalline phases were identified by powder X-ray diffraction (XRD) using RIGAKU-Dmax-2200 PC equipment, operating at 30 kV and 15 mA with Cu–Kα radiation. Both fly ash samples contained both the crystal and the amorphous phase. The crystalline phases generally consist of quartz, mullite, lime, iron oxides, etc. The amorphous phases are predominantly made of aluminum. However, some phases contain silica and silicates containing calcium, magnesium and iron at various concentrations. X-ray patterns and assignment of the peaks of the FA and FA/LB are given in Figure. 2a and Figure. 2b. Ma-



Fig. 3. SEM images of the general view of the SOFA and SOFA/LB (a, b), and of the YFA and YFA/LB (c, d) at different magnification Rys. 3. Obrazy SEM próbek SOFA i SOFA / LB (a, b) oraz YFA i YFA / LB (c, d) przy różnym powiększeniu



Rys. 4. Wyniki oznaczenia odczynu pH

jor crystalline phase of the Seyitömer fly ash was determined as quartz (Figure. 2a). Magnesioferrite is the second dominating mineral. It has small amounts of anorthite, anhydrite, hematite, mullite and lime.

Quartz is found as the major component in the autoclaved SOFA/LB samples. Mullite and lime peaks have disappeared and new phases was occurred such as katoite $(Ca_3Al_2(Si_{0.64}O_{2.56}) (OH)_{9.44})$, tobermorite $Ca_4(Si_6O_{15}) (OH)_2(H_2O)_5$ and calcium silicate hydrate $2CaO(SiO_2)2.4(H_2O)$ (Fig 2a).

As can be seen from Fig. 2b, high content of Quartz (SiO₂) and anorthite (CaAl₂Si₂O₈) were found in YFA. Furthermore, minor amounts of hematite (Fe₂O₃), lime (CaO), gehlenite (Ca₂Al₂SiO₇), anhydrite (CaSO₄), hematite (Fe₂O₃) and mullite (Al₆Si₂O₁₃) were observed. Quartz (SiO₂) was determined as the main crystalline phase of the YFA/LB like SOFA/LB. Similarly, mullite and lime peaks have disappeared in autoclaved YFA/LB samples. Katoite (Ca₃Al₂(SiO₄)1.5(OH)₆), tobermorite and calcium silicate hydrate (CSH) were detected in YFA/LB. The formation of calcium silicate hydrates (CSH), and calcium alumino-silicate hydrates (CASH) occurs as a result of pozzolanic reaction of fly ash with lime. Low alkalinity helps the formation of C-S-H phase while the high alkalinity encourages the poorly crystalline C-(A)-S-H phase formation.

Hollow and spherical particles, which are called as cenospheres and small spherical particles within a large glassy sphere, called plerospheres can be seen in Fig. 3. Some clathrosphere particles with partial melting or eroding on their surface can also be seen in Fig. 3a and 3c.

SOFA, generally composed of irregularly shaped particles and agglomerates, also contains in small amount and different sizes of microspheres and irregularly shaped unburned carbon particles. (Fig. 3a). Particle sizes were observed ranged from submicron to greater than 100 μ m. These findings are well matched with the triple modal size distribution plot of SOFA (Fig. 1a). Results of SEM showed that SOFA also contains many porous particles that the particles contain CAS, anhydride and kaolinite. As seen from the Figure 1a irregular agglomerated form of SOFA composed mainly of CaSO₄, lime and alkali aluminum silicate composites.

It is very different from the structure of SOFA with the individual spherical particles of YFA. Larger parts of the YFA particles consist of spherical and partially agglomerated particles (Figure 3c). In addition, particle size distributions are in the middle narrow range. This finding is consistent with the size distribution given in figure 1b. SEM photos of FA/LB brick are shown in figure 3b and figure 3d. It is observed that after hydrothermal treatment of FA/LB new crystalline phases were formed. The crystalline phases are shaped on the surface of fly ash particles. They cover the surface of fly ash particles in form of short and long needles. These phases are mainly C-S-H in the form of tobermorite and small amount of katoite as determined also by XRD analyses.

3.2. Results of leaching potential of the trace elements in the fly ash/lime brick samples

In this part of the experimental study, typical leaching tests (TCLP 1311, ASTM3987-85 and EN-12457-2) were conducted to determine the solubility of the trace elements in FA/LB under a weak acid and water environment.

ma		SOFA/					EPA max	Waste acceptance criteria, mg/kg at L/S20		
/kg	TCLP	LBs ASTM	EN	TCLP	ASTM	EN	mg/ kg[5 0]	Inert	Nonhaz ardous	Hazardous
As	ND	ND	ND	ND	ND	ND	100	1	4	50
Ba	15.370	0.193	0.206	28.176	11.986	17.843	2000	40	200	600
Ca	25,590	4,220	3,060	82,870	6,880	5,282				
Cd	0.035	0.007	0.047	0.072	0.045	0.020	20	0.08	2	10
Co	2.942	ND	ND	1.3	ND	ND				
Cu	5.447	ND	ND	0.864	ND	ND	300	4	100	200
Cr	8.925	0.244	0.629	1.927	0.101	0.046	100	1	20	140
Мо	0.050	0.027	0.085	1.009	0.498	0.391				
Ni	1.257	ND	ND	0.72	ND	ND	40a	0.8	20	80
Zn	10.391	0.940	0.314	0.430	0.141	0.376	500	8	100	400
Pb	0.1917	ND	ND	0.250	ND	ND	100	1	20	100
Sr	0.30	1.497	1.117	23.371	11.394	9.879				
Fe	872.381	0.45	ND	97.027	0.256	ND				
Hg	ND	ND	ND	ND	ND	ND		0.02	0.4	4
Ti	ND	ND	ND	ND	ND	ND				
Se	ND	ND	ND	ND	ND	ND				

Tab. 3. The concentration of heavy metals in SOFA/LB and YFA/LB leachate (mg/kg) Tab. 3. Zawartość metali ciężkich w odciekach SOFA/LB i YFA/LB leachate (mg/kg)

^a 100x drinking water max, since an EPA-TCLP max has not been established, ND – Not Detected

3.2.1. pH measurements

A number of previous studies indicated that leaching behavior of the elements from fly ash samples can change depending on the pH of the leach solution (Dahl et al, 2008; Iyer, 2002; Valentim et al., 2009; Sasmita et al., 2017). Therefore, the pH values of the samples were continuously monitored during the test. pH variations measured during toxicity tests are illustrated in Figure 4.

During the TCLP tests, pH values of all samples were measured as ranging between 3-5.5 (Figure. 4a). The initial pH of SOFA, YFA and their FA/LBs are found as lower than final pH under TCLP test conditions. . Initial pH values of SOFA and YFA under ASTM D3987 and EN-12457-2 test conditions were found as slightly higher than the final pH values. Both initial and final pH values of samples for ASTM D3987 test were lower than those of EN-12457-2 mainly due to L/S ratio. As seen from Figure. 4b and 4c, the final pH values of the leachate are changing between 12 and 13.5 for both FA in agreement with the free lime content. Final pH of YFA and YFA/LB was slightly higher than that of SOFA and SOFA/LB due to high free CaO content of YFA and YFA/LB. Secondary precipitation reactions can occur in the presence of soluble alkali phases (free calcium oxide, soluble metal salts, oxides and hydroxide) in the test sample. This may bound the solubility of some metals (Akar, 2012; Kim, 2006).

3.2.2. Leachability of toxic elements from autoclaved FA/LB

Fly ash and fly ash derived materials may pose a significant harm to the environment, since some trace elements can contaminate the soil and surface and groundwater, their work is important for environmental protection (Quevauviller et al., 1996; Sloot, 1996). So, the determination of the leaching behavior of trace elements in their form is of prime importance for environ-mental safety.

The leachability of trace elements from the FA/LB samples was investigated using three standard methods (TCLP 1311, ASTM 3987-85 and EN-12457-2). The concentration of the chosen (As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Zn, Pb, Sr, Fe, Hg, Ti, Se) in eluates was analyzed by ICP and experiments are given in Table 3.

The leached element ratios (%) from the fly ash lime brick samples under TCLP (in TCLP test procedure sodium acetate buffer was used at pH 4.99), ASTM D3987 and EN-12457-2 test conditions were given in Figures. 5-6.

Leaching test was performed on FA/LBs showed no presence of Hg, Ti, Ar, Se in investigated samples. Because, in alkaline FA/LB, as release decline with rising pH. In leaching

In terms of the method, it was seen that the elements were higher in TCLP test conditions. Most of the selected trace elements were leached at higher proportions under TCLP test conditions (Figure 5 and Figure 6).

It can be seen from the Figure. 5, Ba, Co, Mo, Zn and Cu leached in weakly acidic media and were solved at higher amounts in SOFA/LB. Cd, Cr, Ni, Sr, and Pb also show solubility but at very little percentages for SOFA/LB. The solubility ratio of metals in TCLP was greater than the solubility ratio of metals in batch leach test (ASTM and EN) due to the metal solubility generally decreases with increasing pH. The leached elements in deionized water because of the batch leaching tests (ASTM and EN) also shown in Figure 5. Ni, Pb, Cu and Cd did not leach from the SOFA/LB. Most of selected elements dissolved relatively low amounts under ASTM and EN test conditions due to the high pH of the medium. The leachability of Pb was found to be very low due to the internal glassy matrix form in the sample therefore not readily leached. It is insoluble and constant, independently from the type of leaching test applied. Cadmium is consistently inert in neutral and alkaline mediums. Even though Cd is connected with the fly ash particles surface, the concentrations leached in water not often exceed the limits (Gould et al., 1989). The leach-ability of Zn is relatively high for SOFA/LB under TCLP test conditions while, in general, Zn mobility for both FA/LB is very low (Figure 5 and 6). Copper (Cu) is present within the glassy phase and not easily released. Leachability of Cu was in between 1.2% and 5.39% under TCLP test conditions while it was not leached in both ASTM and EN (Figure. 5 and 6). Nickel (Ni) is dispersed between the silicate fraction and the magnetic fraction of FA during burning process. The majority of the leachable Ni is released from the non-magnetic fraction. Leached Ni were present in SOFA/LB and YFA/LB under TCLP test conditions, but not present in ASTM and EN.



Fig. 5. Results of TCLP, ASTM D3987 and EN-12457-2 from SOFA/LB. Rys. 5. Wyniki oznaczenia TCLP wg ASTM D3987 i EN-12457-2 w próbce SOFA/LB.



Fig. 6. Results of TCLP, ASTM D3987 and EN-12457-2 from YFA/LB Rys. 6. Wyniki oznaczenia TCLP wg ASTM D3987 i EN-12457-2 w próbce YFA/LB

4. Conclusion

Based on the findings, Seyitomer fly ash sample contains particles below 0.800 mm particle size and 0.212-0 mm fraction makes up 76.06% of the ash. Particle size of Yatagan fly ash sample is found below 0.300 mm and 0.212-0 mm fraction makes up 84.14% of the ash. It is found that both fly ashes have the alkaline character due to lime and soluble metal salts, oxides, hydroxides, and carbonates contents. Quartz (SiO₂) is found as the main crystalline phase, magnesioferrite (Mg-Fe₂O₄) is the second dominating mineral and small amounts of anorthite (CaAl₂Si₂O₈), anhydrite (CaSO₄), hematite (Fe₂O₃), mullite (Al₆Si₂O₁₃) and lime (CaO) was detected in SOFA samples. Quartz is found as the major component in the autoclaved SOFA/LB samples. Katoite (Ca₃Al₂(Si_{0.64}O_{2.56}) (OH)_{9.44}), tobermorite Ca₄(Si₆O₁₅) (OH)₂(H₂O)₅ and calcium silicate hydrate 2CaO(SiO₂)2.4(H₂O) were found in brick samples while mullite and lime peaks in fly ash have disappeared. High content of Quartz (SiO₂) and anorthite (CaAl₂Si₂O₈) were found in YFA with minor amounts of hematite (Fe₂O₃), lime (CaO), gehlenite (Ca₂Al₂SiO₂), anhydrite (CaSO₄), hematite (Fe₂O₂) and mullite (Al₂Si₂O₁₂). Quartz (SiO₂) was detected as the main crystalline phase of the YFA/LB like SOFA/LB.

Both FA/LB showed no presence of Hg, Ti, As and Se in investigated samples. In leaching tests for SOFA / LB and YFA/ LB, the highest solubility was observed in Ba, Cr, Mo, Cd and Co that is the elements with environmental importance. Most of the selected trace elements were leached at higher proportions under TCLP test conditions due to lower pH of the eluate. Using lime in production of fly ash bricks helps to establish an alkaline matrix so that the solubility of many toxic elements are prevented. The release of all trace elements was lower than the hazardous material limit values of waste acceptance for land filling stated in the Annex 2 of the 2003/33/CE Council Decision (based on 1999/31/EC Directive) and TCLP-EPA max directive. The study revealed that there would be no environmental risk posed by the presence of pollutants when SOFA and YFA are used as raw materials in FA/LB-making.

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Wymywalność metali ciężkich z autoklawizowanych cegieł z popiołu lotnego i wapna

Popiół lotny jako uboczny produkt spalania w elektrowniach węglowych stanowi istotny problem ekologiczny. W Turcji w wyniku spalania 40 mln ton węgla brunatnego rocznie powstaje około 15 mln ton popiołów. Na całym świecie podjęto szereg badań w celu wykorzystania popiołu lotnego w celu przezwyciężenia problemów środowiskowych. Jednym z obszarów zastosowania popiołów lotnych jest produkcja cegieł budowlanych. W pracy przedstawiono wyniki badania charakterystyki próbek popiołu lotnego z elektrowni węglowych Seyitomer i Yatagan. Przeprowadzono testy ługowania wybranych pierwiastków śladowych, zgodnie z normami TCLP 1311, ASTM3987-85 i EN 12457-2 na cylindrycznych próbkach popiołu lotnego/ cegieł wapiennych (FA / LB), które zostały wyprodukowane z mieszanek popiołu lotnego i wapna w elektrowniach Seyitömer i Yatagan.

Wyniki pokazują, że uwalnianie wszystkich pierwiastków śladowych było niższe niż dopuszczalne wartości dla materiałów niebezpiecznych. Zatem niewypalane cegły z popiołu lotnego są korzystnym sposobem rozwiązania problemu środowiskowego wpływu usuwania popiołów lotnych.

Słowa kluczowe: popiół lotny z węgla, popiół lotny/cegła wapienna, ługowanie, pierwiastki śladowe



Specification of the Climate Character in the Study Area of Projected Hydric Reclamation

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Abstract

Hydrical reclamation of the residual pit of Most-Ležáky is part of the comprehensive revitalisation of the land affected in the past by mining activity with an area of 1264 ha. Thus, in terms of remediation and reclamation, the most appropriate way to reclaim the residual pit, as one of the final stages of the long-term reclamation activities that have been going on in the area for more than half a century, occurs under the given conditions. The Lake Most, our study area, was planned and created as a hydric recultivation of the former surface Most-Ležáky mine located near the town of Most, in the foothills of the Ore Mountains, approximately 80 kilometers northwest of the capital of the Czech Republic - Prague. The Lake Most represents extensive hydric reclamation, which is unique in the sense that it does not have a natural inflow and runoff, therefore an artificial feeder from the Ohře River had to be built. The main goal of the ongoing research is to construct a mathematical model predicting the water balance of Lake Most. Therefore, it is important to separate amount of water that is lost by the evaporation and amount of water that is lost into the subsoil. If we do not wish to use only temperature equations but more complex methods and equations to calculate evaporation instead, we need to have relative humidity, atmospheric pressure, wind speed, and daylight length values. In addition to the climatic data needed to calculate the evaporation, the amount of precipitation is needed to construct the balance equation of the area. An important objective in planning all hydric reclamations is to ensure their long-term sustainability, which is based on a detailed description of the study area's climate and local hydrological conditions. In our article we focus on assessing the evolution of climate in the area of this hydric reclamation. We have processed a long-term series of measurements in monthly averages from the Kopisty meteostation data provided by the Institute of Atmospheric Physics of the CAS.

Keywords: climate, evaporation, hydric reclamation, Lake Most

Introduction

The issue of free water surface evaporation is highly topical in relation to the sinking of pits after surface mining, given the nature of the weather in recent years. The impact of water surface evaporation on the overall hydrological balance of a river basin can be significant, especially in years with low annual precipitation. Currently, the increasing air temperatures appear to be the biggest problem, resulting in increased territorial as well as water surface evaporation. These water losses from the hydrological system are not sufficiently compensated by annual precipitation, which is unevenly distributed across the territory of the Czech Republic, and thus there are areas in the Czech Republic where the total evaporation exceeds precipitation and drought effects can be observed, see, e.g. (Beran & Hanel, 2015).

Basically there are five methods of determining evaporation: water budget method, mass transfer method, energy budget method, pan evaporation method and combined method, see (Brutsaert, 2005), (Maidment, 1993). Each of these methods could yield different equations despite the basic ideas being the same. This could be caused by different approaches to determination of involved empirical constants and coefficients (Dlouhá & Dubovský, 2019).

Characteristics of the area

Our study area, Lake Most (Fig.1) was created by the hydric recultivation of Most – Ležáky quarry, which was situated in the

central part of the North Bohemian brown coal basin. Before the flooding of the area of the residual pit a whole lot of sanitation works had to be done, such as building sewerage of the future lake, construction of the underground sealing wall, construction of the banks, according to the law in the Czech Republic. All these landscape interventions were done with respect to the future usage of the lake (Dlouhá & Dubovský, 2019). The Lake Most is a closed system without natural inflow or outflow. The residual pit of the lake was filled through a feeder from Nechranice industrial water pipeline from the Ohře River in 2008-2014. The current lake area is 309.4 hectares with a water volume of 70.5 million cubic meters and a maximum depth of 75 meters. Until September 2020, the waterworks was operated in the validation regime, now it serves as a recreational area.

Materials and methods

We have processed a long-term series of measurements in monthly averages from the Kopisty meteostation data provided by the Institute of Atmospheric Physics of the CAS. The results in annual averages are complemented by a trend as well as a regression line. The trend line is a line drawn over pivotal heights or below the pivotal minimum that indicates the predominant direction of the quantity to be monitored. The regression line is interspersed with a set of pivotal heights.

The trend is not unequivocal when comparing annual precipitation totals (Fig. 2). Using the trend line (a), its variation



Fig. 1. The Lake Most Rys. 1. Jezioro Most

with the variation in annual precipitation can be seen. If the regression line is used, there is an upward trend (b).

Temperature processing results indicate that the average annual temperature (Fig. 3) is increasing in trend using both the trend line (a) and the regression line (b). This rise is estimated to be 2°C, for the reporting period 1970-2018.

Annual wind speed averages (Fig. 4) fluctuate greatly, so does the trend line (a). However, when the regression line (b) is intersected, we can talk about a small decrease.

The comparison of annual sunshine averages (Fig. 5) clearly shows an increasing trend using both methods (a), (b).

Moisture, which has been on a sustained trend throughout the monitored period, has experienced fluctuations in recent years (Fig. 6) which are followed by the trend line (a). In a linear regression, the line is slightly rising (b), despite the evaporation being more subnormal in recent years.

Comparison of annual evaporation $\rm E_{\rm th}$ from the Kopisty meteostation data in the period 1970-2018

Data from 1970-2018 is available in monthly averages. Therefore, the Thornthwaite method for the month step (1) was chosen to calculate the evaporation.

The Thornthwaite method is the most frequently cited method for determining evaporation. A more detailed description of the method can be found in books (Wilson, 1974), (Davie, 2008), or (Gerosa, 2011). In those books reference is made to an article (Thornthwaite, 1948) in which Thornthwaite derives the formula and further uses it to classify the climate, i.e. to divide it into perhumid, humid, moist subhumid, dry subhumid, semiarid and arid regions.

It uses a monthly or annual temperature index to determine the monthly evaporation rate alone, $i_m = (Ta_m)/5)^{1,514}$ resp. $I=\Sigma^{12}_{m=1} i_m$, where Ta_m , where Ta_m is the average air temperature in the m-th calendar month. The annual temperature index I is thus calculated from the long-term/monthly temperature averages of Ta_m for the whole year. In the calculation of E_{Th} itself, Ta_m indicates the average air temperature in the month in which we are to determine the evaporation and the resulting E_{Th} value corresponds to the evaporation in millimetres per month (mmm⁻¹).

In months in which the average temperature of Ta_m is negative, the monthly index i_m shall be set equal to zero, and so shall E_{Th} itself be zero in that case. For positive Ta_m values, the monthly total of evaporation E_{Th} is calculated as follows:

$$E_{TL} = (10T_{-})/I)^{675.10^{-9}I^{3}-771.10^{-7}I^{2}+1792.10^{-5}I+0,49239}$$
(1)

Since this is a temperature equation, we can see a similar trend and increase as for temperature (Fig.7).

Comparison of the annual evaporation E_Rom from the Kopisty meteostation data from the period 1970 – 2019

The Romanenko method (2) is, after the Thornthwaite evapotranspiration determination method, another method that works in a monthly step. It is described by the following relationship

$$E_{\text{Rom}} = 0,0018 \cdot (100 - \text{RH}) \cdot (25 + T_a)^2$$
(2)

where T_a and RH denotes average air temperature and relative air humidity, respectively.

As in the case of Thornthwaite, we can see an increasing trend in evaporation in Romanenko, even though this equation depends not only on temperature but also on humidity (Fig. 8).

Results and discussion

The research team, which was established thanks to the support of the "CzechAdapt - System for the exchange of information on climate change impacts, vulnerability and adaptation measures in the Czech Republic" project published their prediction of the future development of climate conditions on the project's website (www.ecosystemservices.cz).

A comparison of the average annual precipitation averages for the period 1970-2018 and the forecasts for the period 2021-2100 show that the amount of precipitation should be similar. However, the average air temperature will rise.

When assessing the amount of water in our landscape, we have to take into account that the extremes of precipitation have become increasingly dynamic in recent years. The increase in air temperature over the period from 1970 to 2018 is demonstrable, but the steady state of annual precipitation is statistically confirmed. These findings indicate that the frequency of droughts may be increasing, as evidenced by these evaluations.

Compared to the averages of temperatures and precipitation in the Czech Republic, the area of planned hydric reclamation is situated in an area of severely above-normal average annual temperature, a strongly sub-normal total of precipitation and a sub-standard number of hours of sunshine.

Each area has its own specific conditions and is also different within a single study area. The reason why it is important to have the best measured climate data in a long-enough time series is captured by the graph (Fig. 9) showing the percentage increase in annual evaporation if the average temperature increases by 1 degree and if it increases by 3 degrees.

Since we have daily step data for 2014-2018, we were able to determine the effect of temperature rise on free water surface evaporation using the Penman – Monteith equation, which works with daily step data.


Fig. 2. Comparison of the annual precipitation based on the data from the Kopisty meteostation in 1970 – 2018 supplemented with the trend line (a) and the regression line (b)

Rys. 2. Porównanie opadów rocznych na podstawie danych z meteostacji Kopisty w latach 1970 - 2018 uzupełnionych o linię trendu (a) i linię regresji (b)



Fig. 3. Comparison of the annual temperature averages from the Kopisty meteostation data from the period 1970-2018 supplemented with the trend line (a) and the regression line (b)

Rys. 3. Porównanie rocznych średnich temperatur z danych meteorologicznych Kopisty z lat 1970-2018 uzupełnionych o linię trendu (a) i linię regresji (b)



Fig. 4. Comparison of the annual wind speed averages from the Kopisty meteostation data from the period 1970-2018 supplemented with the trend line (a) and the regression line (b)

Rys. 4. Porównanie rocznych średnich prędkości wiatru z danych meteorologicznych Kopisty z lat 1970-2018 uzupełnionych o linię trendu (a) i linię regresji (b)



Fig. 5. Comparison of the annual sunshine averages from the Kopisty meteostation data from the period 1970-2018 supplemented with the trend line (a) and the regression line (b)

Rys. 5. Porównanie rocznych średnich nasłonecznienia z danych meteorologicznych Kopisty z lat 1970-2018 uzupełnionych o linię trendu (a) i linię regresji (b)



Fig. 5. Comparison of the annual sunshine averages from the Kopisty meteostation data from the period 1970-2018 supplemented with the trend line (a) and the regression line (b)

Rys. 5. Porównanie rocznych średnich nasłonecznienia z danych meteorologicznych Kopisty z lat 1970-2018 uzupełnionych o linię trendu (a) i linię regresji (b)



Fig. 7. Comparison of the annual evaporation E_{1n} from the Kopisty meteostation data from the period 1970-2018 supplemented with the trend line (a) and the regression line (b)

Rys. 7. Porównanie rocznego E₁₇, parowania z danych meteorologicznych Kopisty z okresu 1970-2018 uzupełnionych o linię trendu (a) i linię regresji (b)



Fig. 8. Comparison of annual evaporation E_{Rom} from the Kopisty meteostation data for the period 1970 – 2018 supplemented with the trend line (a) and the regression line (b)

Rys. 8. Porównanie rocznego E_{Rom} parowania z danych meteorologicznych Kopisty z okresu 1970 - 2018 uzupełnionych o linię trendu (a) i linię regresji (b)



Fig. 9. Percentage increase in annual evaporation Rys. 9. Procentowy wzrost rocznego parowania

In the work (Allen et al., 1998) FAO (Food and Agriculture Organization of the United Nations) recommended The Penman-Monteith equation in the form (3) as standard estimation method.

$$E_{FAO} = \frac{0.408\Delta(R_n - G) + \gamma \frac{900}{T_a + 273} u_2(e_s - e_a)}{\Delta + \gamma(1 + 0.34u_2)}$$
(3)

The E_{FAO} denotes the evapotranspiration intensity in mmd⁻¹ and it is calculated using the following variables and constants. The term Δ represents the slope of the water vapor saturation curve at a given air temperature, R_n is the net radiation on the surface, and G is the heat storage change in soil or in water, both R_n and G are expressed in MJm⁻² d⁻¹. According to Linacre article (Linacre, 1993) for daily or monthly estimates of the evaporation rate of free water level the term G can be neglected, i.e. set G=0. The term ($e_s - e_a$) in kPa, is the difference of saturation vapor pressure and actual vapor pressure, u_2 denotes wind speed in height 2m above surface in ms⁻¹. The constant γ depends on atmospheric pressure P in kPa, T_a is air temperature in °C.

Conclusion

A long-term series of climate data shows that the average annual air temperature in the period 2014-2018 increased by about 2°C in comparison with the period 1970-2013. As a result, free water surface evaporation is 5-6% higher. Simulating and predicting the further development of the hydrological balance of the study area following precipitation and air temperature scenarios for future periods and assessing the impact of climate change scenarios on the hydrological balance of the pilot area is therefore an essential part of preparing planned hydric reclamation. This is the only way to estimate the expected free water surface evaporation and use it to establish a long-term sustainable water balance in the study area.

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Określenie charakterystyki klimatu w badanym obszarze projektowanej rekultywacji wodnej Jezioro Most jest wyjątkowe w tym sensie, że nie ma naturalnego dopływu i odpływu, dlatego konieczne było wybudowanie sztucznego dopływu rzeki Ohře. Głównym celem prowadzonych badań jest zbudowanie modelu matematycznego prognozującego bilans wodny jeziora Most. Dlatego ważne jest, aby zbilansować ilość wody traconej w wyniku parowania od ilości wody traconej do podłoża. Poza zależnościami od temperatury, wykorzystano bardziej złożone metody i równania do obliczenia efektu parowania, uwzględniające wartości wilgotności względnej, ciśnienia atmosferycznego, prędkości wiatru i długości dnia. Oprócz danych klimatycznych potrzebnych do obliczenia parowania, w równaniach bilansu uwzględniono ilość opadów. Ważnym celem przy planowaniu rekultywacji wodnej jest zapewnienie długoterminowej trwałości, co opiera się na szczegółowym opisie klimatu i lokalnych warunków hydrologicznych badanego obszaru. W naszym artykule skupiono się na ocenie ewolucji klimatu w badanym obszarze rekultywacji wodnej. Przetworzono serię długoterminowych pomiarów w średnich miesięcznych z danych meteorologicznych Kopisty dostarczonych przez Instytut Fizyki Atmosfery CAS.

Słowa kluczowe: klimat, parowanie, rekultywacja wodna, jezioro Most



Stabilizing Na-bentonite by Poly(Diallyl Dimethyl Ammonium Chloride) Adsorption

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Abstract

Clay minerals have been modified by polymers for different applications. The polymer addition affects not only the surface properties but also the rheological properties and the stability of the clay-polymer suspension as a whole. In the current study, the electro-chemical properties of bentonite particles in presence of poly diallyl dimethyl ammonium chloride (PDDACl) were investigated. These properties were characterized by as zeta potential, adsorption isotherm, Fourier transform infrared (FTIR) and the apparent viscosity at different solid percent. The results indicated that the viscosity of the bentonite-PDDACl suspension not only increases by raising the polymer concentration but also by increasing solids %. Adsorption of PDDACl polymer increases the positivity of bentonite surface as a function of polymer concentration, which could be explained mainly by electrostatic interaction of deficient metal ions at the octahedral sheets of bentonite with the cationic head group of the polymer. The PDDACl adsorption isotherm on bentonite fits more probably Langmuir than Freundlich isotherm.

Keywords: bentonite, clay, cationic polymer, Poly(diallyl dimethyl ammonium chloride), viscosity

1. Introduction

Most of the industrial applications of clay minerals depend on the adsorption of polymers on clay raw material [1-3]. The clay- polymers interactions modify the physico-chemical properties of the clay particles. Surface charge, surface active sites and functional groups, rheology and suspension dispersibility are the most important for industrial and technological prospective [4-5]. Several types of polymers of different ionic characters and even non-ionic polymers were applied to modify the clay suspension properties [6-7]. The electrokinetic and rheological properties of different types of clays in presence of salts, surfactants and polymers are the subject of various studies [8-12].

The interaction of polymer functional groups to clay surface significantly affects the interfacial and flow characteristics of the clay-polymer suspension. A great number of studies focused on the adsorption of polymers on kaolinite, which has 1:1 layer structure with low exchange capacity and minimal layer charge. On the other hand, the montmorillonite, smectite group, attract more attention due to its 2:1 layer structure with high exchange capacity and high layer charge [13-16].

Treating the montmorillonite with cationic polymers is one of the promising techniques not only to control the surface charge but also its reversal as well as changing its rheological properties. However, the cationic polymer effect depends mainly on the intrinsic polymer characteristics such as molecular weight and its function groups. Poly (diallyl dimethyl ammonium chloride) is one of widely used cationic polymers in the industry. For instance, the adsorption of Poly (diallyl dimethyl ammonium chloride) onto kaolinite and its effect on its electrokinetic and rheological properties was investigated [17]. Therefore, the aim of the current study is investigating the adsorption of Poly (diallyl dimethyl ammonium chloride) onto bentonite, as a different structure from kaolinite, was investigated using adsorption, Fourier Transform Infra-Red (FTIR), apparent viscosity and electro-kinetic (zeta potential) measurements. The effect of such bentonite-polymer interaction on the suspension stability in terms of electrical and rheological properties was discussed. In addition, the adsorption trend was fitted to Langmuir and Freundlich isotherms and the adsorption mechanism was highlighted.

2. Experimental

2.1. Materials

2.1.1. Clay

The bentonite sample was kindly provided by "Egypt bentonite and derivatives Co.", Western Desert, Egypt. The selection of this locality was mainly because of the presence of high proportion of montmorillonite with the lowest amount of impurities.

2.1.2. Polymer

Poly (diallyldimethylammonium chloride), (C8H16ClN) n, was obtained from Sigma-Aldrich Co. (USA) with average molecular weight (Mw ~100,000-200,000), Figure 1. The polymer solution was prepared at 3% in bi-distilled water. The reagent grade HCl and NaOH were used as pH modifiers.

2.2. Methods

2.2.1. Viscosity Measurements

Bentonite suspensions of (4-10% w/w) were prepared in de-ionized water as well as with different polymer concentrations (0, 20 and 60 mg/l) at constant temperature (25.0 \pm 0.5°C) after 24 h of mixing at 600 rpm to determine the sus-

Tab. 1. Chemical analysis of the bentonite sample Tab. 1. Analiza chemiczna próbki bentonitu

Component	%
SiO ₂	52.49
Al ₂ O ₃	21.58
Fe ₂ O ₃	10.82
TiO ₂	1.56
CaO	0.42
MgO	3.21
Na ₂ O	0.84
K ₂ O	0.41
P ₂ O ₅	0.09
Ignition loss	8.56
Total	99.98

Tab. 2. Size distribution of bentonite sample
Tab. 2. Rozkład wielkości próbki bentonitu

	Particle size, µm	% Retained		
Γ	+100	0.12		
	-100+74	2.56		
	-74+53	38.18		
	-53+45	36.89		
	-45+32	16.94		
	-32+20	3.76		
	-20+10	0.98		
	-10	0.57		

Tab. 3. Isotherms model constants and correlation coefficient (R2) Tab. 3. Stałe modelu izoterm i współczynnik korelacji (R2)

Isotherm model	Isotherm constants			
Langmuin	q _{max}	b	R ²	
Langmuir	1.1223	0.1828	1.00	
European difficile	K _f	N	R ²	
Freundlich	42.10	0.51	0.9747	

pension apparent viscosity. The apparent viscosity, in centipoise, was determined by a Capillary Rheometry Units RH-10 (Malvern Instruments CO., USA) and calculated by dividing rotational viscosity at 600 rpm (R600) by 2.

2.2.2. Zeta Potential Measurements

The zeta potential measurements of bentonite were performed in absence and presence of polymer using a "Zeta-meter system 3+ unit (Zeta-meter Inc., USA). A bentonite sample of 0.1 g was added to 50 ml of definite electrolyte concentration at ionic strength of 10^{-2} M NaCl. The pH was adjusted to the required value with either NaOH or HCl solutions. In the case of using polymer, the required polymer concentrations were added. The suspension was shaken for 30 min then it was transferred to zeta-meter for measurement. Five measurements was taken and averaged to represent the zeta potential at certain pH.

2.2.4. Adsorption Measurements

Experiments were carried out using 0.5 g bentonite in 100 ml of cationic polymer solutions ranging in equilibrium concentration from 0 to 20 mg/L. Solutions were shaken for 8 h at 25°C. After centrifugation at 7500 rpm for 20 minutes, decanted solutions were filtered from a 0.45-µm membrane filter. The total organic carbon content (TOC) in the supernatant was determined using a "Phoenix 8000" Total Carbon Analyzer (Teledyne Instruments - Tekmar, USA).

2.2.5. FTIR Measurements

The FTIR spectra of clay and clay-polymer interactions were recorded by FTIR spectrophotometer (FTLA 2000 Model) using potassium bromide (KBr) disk method in the range of 400–4000 cm–1 at a resolution of 2 cm⁻¹. The FTIR spectra of Poly (diallyl dimethyl ammonium chloride), PDDACl, were examined using FTIR-ATR spectrometer (Scimatar-1000, Varian Associates Inc., USA).

3. Results and Discussion

3.1. Characterization of Bentonite Clay

Table 1 shows the chemical analysis of the used bentonite sample. The Al_2O_3/SiO_2 ratio and the ratio of Na_2O/CaO , from Table 1, reveal that the sample is Na-bentonite rather than Ca-bentonite [18-19]. The reasonably high loss-on-ignition (L.O.I) value (>8%) indicates the higher montmorillonite content. In addition, Table 2 shows the size distribution of the bentonite sample where about 60% of the sample is - 53 μ m.

3.2. Zeta Potential

The change in zeta potential of Na-bentonite as a function of pH in the absence and the presence of PDDACl is presented in Fig.2. The iso-electric point (iep) of Na-bentonite before the addition of PDDACl seems to be at highly acidic pH (between pH value 1 and 2, not shown in the figure) which coincides with iep values reported for similar clays [20]. After adding PDDACl, as a cationic polymer, the zeta potential moves to the positive potential values. The zeta potential of polymer treated Na-bentonite slightly decreases with increasing pH values. The most important observation is the shift of iep of the Na- bentonite after adding the polymer.

In addition, changing the polymer concentration at pH 7 was studied, Fig.3. It is noticed that increasing the polymer concentration shifts the zeta potential from negative value (-36 mV) at no polymer additions to positive value (10 mV) at 10 mg/L polymer concentration. At polymer concentra-

Tab. 4. The characteristic peaks for bentonite and PDDAC polymer Tab. 4. Charakterystyczne piki dla bentonitu i polimeru PDDAC

Material	Peaks wave number,	Description	References
	cm ⁻¹		
Bentonite	3630	O–H stretching	[23-24]
	3443	interlayer and intralayer H-bonded O-H	
	3200 -3500	Si-O and AI-O	
	1640	H-O-H bending	
	1035	Si-O stretching	
	916-and 626	Al-OH vibration	
	915 and 843	Al-O stretching	
	519 and 466	Si-O-Al modes	
PDDAC	3742	O-H stretching	[25]
Polymer	2992 and 1541	stretching and bending vibrations of methyl	
-	2920 and 1397	stretching and bending vibrations of methylene	
	1692	vibration of quaternary ammonium group	
	1653	OH bending vibration of water	
	1147 and 1057	skeletal vibration mode of C-C groups	
	679	rocking mode of CH ₂ groups	



Tab. 4. The characteristic peaks for bentonite and PDDAC polymer Tab. 4. Charakterystyczne piki dla bentonitu i polimeru PDDAC

tion between 10 mg/L and 60 mg/L, the zeta potential increases gradually until it reaches a constant value (about 70 mV). Achieving a constant potential may be attributed to the balance between positive charges of polymer molecules and negative charges on the bentonite surface, which indicates the electrostatic nature of polymer adsorption. In addition, such balance indicates the formation of polymer monolayer at the bentonite surface, which suggest the Langmuir type of adsorption.

3.3. Apparent Viscosity

Addition of solid particles to fluid affects the suspension viscosity due to the interaction between solid particles and fluid molecules, which consequently obstruct the flow and its velocity gradient [21]. Keeping the shear-force constant, the viscosity increases with increasing the solid content as shown in Fig.4. It is clear that increasing the solid content increases the apparent viscosity due to increasing the volume occupied by the solid particles as can be indicated by Einstein's equation, eqn (1) [22]:

$$\mu_r = 1 + 2.5 \ \varphi \mu_r = 1 + 2.5 \ \varphi \tag{1}$$

or even modified equation proposed by Guth and Simha, eqn (2) [23]

$$\mu_r = 1 + 2.5 \ \phi + 14.1 \ \phi \mu_r = 1 + 2.5 \ \phi + 14.1 \ \phi^2 \eqno(2)$$

Where,

 $\mu_r \mu_r$ is the relative viscosity (dimensionless), $\phi \phi$: solid volume fraction.

It is also worth mentioning that the increase in viscosity with increasing both of solid content and polymer dosage reveals the polymer role in dispersing the solid particles by electrostatic repulsion between the particles as confirmed by zeta potential.

3.4. FTIR

Figure 5 shows the bentonite characteristic peaks before and after using PDDAC. The main peaks for bentonite and polymer are listed in Table 4. The FTIR spectra show that the position of OH groups on bentonite surface does not show significant change after the bentonite - polymer molecules interaction. In addition, the adsorbed water molecules onto bentonite peaks at 3453 and 1642 cm⁻¹ insignificantly shifted to 3441 and 1648 cm⁻¹ for bentonite–PDDACl system, respectively. Conclusively, the bentonite spectra after treatment with polymer is the summation of the individual peaks for bentonite and polymer which indicates the physical interaction, mainly by electrostatic interaction, between them. [17].

3.5. Adsorption Isotherm

Figure 6 shows the adsorption isotherm of PDDACl onto bentonite at room temperature (25°C) and pH 7. The adsorption isotherm of PDDACl onto Na-bentonite shows a gradual increase in the adsorption density with concentration. The shape of the adsorption isotherm indicates the physical adsorption through following the L-type isotherm in which the slope decreases with increasing the polymer concentration due to the limited vacant adsorption sites [26].

The presence of multivalent cations such as Ca and Mg ions in the structure of bentonite, as substitution to Si and Al ions in tetrahedral siloxane sheets and octahedral alumina sheet, results in reducing the net positive charge or increases the negative charge [27]. Taking into account that the PDDA-Cl is cationic polymer therefore, it will be electrostatically attracted to surface negative charge on the bentonite particles, where the adsorption depends on simultaneous interaction between cations in the polymer and the anions on the bentonite surface [28-29].

Therefore, Fig.6 reveals that the adsorption of PDDACl as a cationic polymer starts initially due to electrostatic attraction and the adsorption intensity increases by increasing



Fig. 2. Zeta potential of bentonite before and after adsorption of polymer in 0.01 M NaCl solution (at 10 mg/L polymer concentration) Rys. 2. Potencjał Zeta bentonitu przed i po adsorpcji polimeru w 0,01 M roztworze NaCl (przy stężeniu polimeru 10 mg/L)



Fig. 3. Zeta potential of bentonite in presence of polymer in 0.01 M NaCl solution at pH 7 Rys. 3. Potencjał Zeta bentonitu w obecności polimeru w 0,01 M roztworze NaCl przy pH 7



Fig. 4 Effect of polymer additions on the apparent viscosity of bentonite clay at different solid content Rys. 4. Wpływ dodatków polimerowych na lepkość pozorną glinki bentonitowej przy różnej zawartości części stałych

the polymer concentration due to the high cation exchange capacity of montmorillonite.

In addition, the polymer-/bentonite interaction was analyzed by Langmuir and Freundlich isotherms as shown in Figs. 7 and 8, respectively. These isotherms have been frequently used to identify the adsorption behaviour of bentonite and other materials [30-31]. The linear forms of both adsorption isotherm models are given by the equations 1 and 2:

Langmuir
$$Ce / q = Ce / K_1 + 1 / K_1 K_2$$
 (3)
Freundlich $\log q = \log K_1 + N \log C$ (4)

where, Ce (mg/L) is the equilibrium concentration of polymer, q (mg/g) is the adsorbed amount per unit mass of bentonite, K_1 (mg/g) indicates the maximum adsorption capacity of the polymer onto clay, and K_2 (L/mg) is an index of adsorption energy. K_{ϵ} (L/kg) and N denote the monolayer sorption capacity and sorption constant, respectively. In addition, Table 3 shows the isotherms constants and their correlation coefficient. It is clear from Figs. 7 and 8 that the PDDACl on bentonite follow the Langmuir (monolayer) adsorption mechanism.

4. Conclusions

Adsorption of PDDACl onto bentonite clay was studied. Adsorption isotherm, zeta potential, FTIR and apparent viscosity measurements were used to clarify the adsorption mechanism. The characterization of clay sample indicated that the sample is Na-bentonite with mean size of 50 microns. The results of adsorption isotherm, zeta potential and viscosity, as a function of solid content, indicated that the adsorption of polymer depends mainly on the electrostatic interaction where the positive functional groups of the polymer attach to the negative bentonite surface. In addition, the



Fig. 5. FTIR spectrum of bentonite, cationic polymer and treated bentonite Rys. 5. Widmo FTIR bentonitu, polimeru kationowego i bentonitu poddanego obróbce



Fig. 6. The adsorption isotherm of cationic polymer on bentonite at pH Rys. 6. Izoterma adsorpcji polimeru kationowego na bentonicie przy pH



Fig. 7. Langmuir isotherm for polymer adsorption on bentonite Rys. 7. Izoterma Langmuira dla adsorpcji polimeru na bentonicie



Fig. 8. Freundlich isotherm for polymer adsorption on bentonite Rys. 8. Izoterma Freundlicha dla adsorpcji polimeru na bentonicie

increase in the viscosity with increasing the solid content reveals the role of the polymer in dispersing the solid particles into the liquid phase, which confirms the electrostatic repulsion between bentonite particles especially in the presence of polymer. Such bentonite-polymer interaction modifies the bentonite slurry rheological properties to be suitable for its usage as a drilling mud. In addition, controlling the charge on the bentonite particles by adding the polymer results in its usage in mining industry, paper industry as well as the waste water dewatering.

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Stabilizacja Na-bentonitu przez adsorpcję poli (chlorku diallilodimetyloamoniowego)

Minerały ilaste zostały zmodyfikowane przez dodatek polimerów do różnych zastosowań. Dodatek polimeru wpływa nie tylko na właściwości powierzchni, ale również na właściwości reologiczne i stabilność zawiesiny glina-polimer jako całości. W niniejszej pracy zbadano właściwości elektrochemiczne cząstek bentonitu w obecności chlorku polidiallilodimetyloamoniowego (PD-DACI). Właściwości te scharakteryzowano jako potencjał zeta, izotermę adsorpcji, podczerwień z transformacją Fouriera (FTIR) oraz lepkość pozorną przy różnych zawartościach fazy stałej. Wyniki wskazały, że lepkość zawiesiny bentonit-PDDACl wzrasta nie tylko wraz ze wzrostem stężenia polimeru, ale także ze wzrostem udziału fazy stałej. Adsorpcja polimeru PDDACl zwiększa dodatniość powierzchni bentonitu w funkcji stężenia polimeru, co można tłumaczyć głównie oddziaływaniem elektrostatycznym deficytowych jonów metali na oktaedrycznych arkuszach bentonitu z kationową grupą polimeru. Izoterma adsorpcji PDDACl na bentonicie pasuje bardziej do izotermy Langmuira niż izotermy Freundlicha.

Słowa kluczowe: bentonit, glina, polimer kationowy, Poli(chlorek diallilodimetyloamoniowy), lepkość



Financing Sources of Exploration Works in the Light of Risk Related to their Activity

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Abstract

The article presents an overview of the determinants of exploration works and the definition of the role of junior mines in those processes. Junior mines, as special purpose vehicles, focus on the stages of exploration and documenting of the deposits, without going into the operational stage related to the exploitation. Due to their nature, those entities finance their activities with equity capital in the form of share issues on the capital markets, addressing their proprietory securities to investors who accept a high level of risk. The largest stock exchanges on which the exploration companies obtain the required funds have been identified, and the trends that complement capital raising, concerning the involvement of private equity funds, have been presented.

Keywords: mining, exploration, junior mines, financing

1. Introduction

Mining industry constitutes one of the primary sectors of economic development, especially in developing regions such as Africa and South America, where it is export leverage supporting the needs of developed economies. Such economies, which are based on modern and innovative sectors, utilise the resources obtained and processed in the complex production processes in the electronics and automotive industries. Japan is one of the examples, as even though it does not have mineral resources of its own, it is still the world's biggest consumer of mineral resources, importing them from various parts of the world. Similar trends are also present in France [1]. Among developed countries, Australia is a unique phenomenon. Although the country is among the world's nine richest economies, it is the mining industry that its economic prosperity and the gross domestic product growth are based on.

The demand for raw materials has been increasing since the beginning of the twentieth century and based on the forecasts for 2050, it is unlikely to decrease [11]. Given the historical consumption trends, one should assume that the extraction of natural resources will actually increase. According to Global Resources Outlook, today's consumption trends indicate that the extraction of such resources as metal ores will be increasing by about 1.7% annually until 2060 [2]. This demand can only be met by increasing the production output of the already existing mines [7]. However, it is possible that with the current technological developments, the constant demand for mineral resources could also be met through the exploitation of the so-called anthropogenic deposits, including mining waste storage sites [3], as well as small deposits [4]. Although recycling methods are also being refined to help meet the demand for metals, they only supply a limited amount of them [4].

Therefore, obtaining and making new deposits of raw materials available to support the needs of modern and innovative economic processes is becoming a necessity if the further development of advanced technologies is to take place. This goal is achieved through explorations as well as through mergers and takeovers of deposits that have already been documented, which are effective alternatives to launching new geological-mining projects and providing the necessary raw materials.

Looking at the entire life cycle of the geological and mining projects, it should be remembered that it often takes many years from a discovery of a deposit to mass production [8], therefore the risk associated with them is usually multifaceted. The specificity of the works seems to justify the need for an individual approach to the problem of a proper selection of funding sources [12] and matching them to a specific stage of advancement in the whole life cycle. When analyzing the risk related to such a project, it should be noted that the risk varies and decreases with the progress of work. Undoubtedly, when analyzing the life cycle of a geological-mining project, the greatest risk of failure, and thus of incurring outlays which will not bring the intended economic effects, are the processes related to the exploration of the deposit and its estimation. The characteristics of such works in conjunction with their capital intensity is an interesting topic related to the selection of funding sources as well as the economic efficiency of the activities carried out in the context of the whole geological-mining project.

The market analyses confirm that there is currently a strict specialization that consists in shifting exploration works from large mining companies to junior mines, i.e. special purpose vehicles involved in such activities.

In the context of the above-mentioned issues, this article aims to present the funding sources of exploration works in the light of their specificity and conditions, which at the same time justify and legitimize the functioning of the special purpose vehicles, i.e. junior mines. Such entities are often listed on alternative capital markets where they try to raise funds for their activities



Fig. 1. Mine life cycle stages [22] Rys. 1. Fazy cyklu życia projektu geologiczno-górniczego

2. Materials and Methods

For the purposes of this publication, a literature review was carried out to present the role of junior mines companies in the processes of carrying out exploration works. The publications were searched for using several search engines such as: Science Direct (Elsevier), Scopus or Gate Research. Each of them gave different search results. Terms such as "junior mines", "life cycle", "financing" and "stock exchange" were used to search for "title", "keyword" and "summary" of the indexed literature field. Initial searches and research in search engines resulted in a total of 136 publications that were of interest to the authors of this publication.

In the next step, a selection of publications was made, rejecting those that were not relevant to our questions and research considerations regarding the role of junior mines companies and sources of financing for exploration works. As a result, the focus was on 35 publications (including 16 articles and 16 reports) constituting the final dataset. On their basis, the characteristics of special purpose vehicles of the juniors mines type, exploratory works being part of the geological and mining project life cycle and financing of these works, taking into account the mine development phases, were made. Most of them were published between 2019-2020. A large part of them, in terms of geography, is related to Canada (TSV-X), Great Britain (AIM) and Australia (ASX), because there are the largest stock exchanges on which juniors are listed. These countries attracted mining companies to their financial market, providing opportunities for them to accumulate capital and develop them in the field of mining and related industries.

3. Results

In this section, the main results are described starting with the characteristic of effects in exploration work. Subsequently, it was presented the main type of enterprises, which are identified as junior mines. They carry out the explorations works, becoming the specialist ones in these processes.

3.1. The characteristics of effects in exploration works

Extraction works are part of a geological-mining project life cycle and constitute its vital element, as they determine its subsequent stages. The project life cycle is defined within the time horizon determined by the beginning and the end of a project.

A geological-mining project can be defined as activities carried out in the mining industry such as searching, sharing, extraction, dressing of the minerals and selling the enriched product [23]. The implementation of such a project is related to a mineral deposit, the extraction of which is the object of the operating activity of a mining company. Mineral deposits are very characteristic, which is evidenced by the rarity and the uniqueness of their occurrence both in terms of geological conditions as well as their location, non-renewability and uncertainty about the construction of resources and geological characteristics. Therefore, implementation of the geological-mining project is not only related to finding a deposit but also to obtaining licenses and permits to extract them. Implementation of such a project differs from the implementation of any other project in technical, technological and financial terms. The particularly distinctive features include [24]:

- long pre-production period which consists of searching for deposit and its evaluation, sharing and preparing for mining,
- long mining period,
- complex geological-mining conditions,
- high capital intensity,
- high cost of capital financing the project (long payback periods),
- production inflexibility,
- high operational risk (high fixed operating costs),
- price unexpectedness on natural resources market.

Therefore, the implementation of the discussed geological-mining works consists of several stages: exploration and recognition of mineral deposits, evaluation of a deposit,



Fig. 2. The relationship between the investment risk and the stage of a mining and geological project's life cycle. Source: own study Rys. 2. Zależność pomiędzy ryzykiem inwestycyjnym a fazą cyklu życia projektu geologiczno- górniczego



Fig. 3. Changes on the global mining market at the beginning of the 21st century [35] Rys. 3. Zmiany na światowym rynku górniczym od początku XXI wieku

building a mine, land exploitation and enrichment as well as liquidation and reclamation [25].

As a part of the exploration stage, the deposit is exposed and the mineral deposit is documented. The next stage, the assessment of the deposit, is reached by approx. 5% of the projects implemented in the exploration stage [26]. The analyses carried out in this stage are aimed at identifying the parameters that characterize the deposit. The works focus on determining whether the extraction of mineral resources is technically feasible and commercially reasonable (feasibility study). This stage ends with a decision to build the mine. This is the most capital-intensive stage, which requires the investor to obtain several permits, which may result in extending the stage in time. It requires identification of complete assets that would be fit for use and would ensure the exploitation at the level of the designed extraction capacities. After the mine is constructed and the preparation of the deposit for exploitation is completed, the mining production begins. The production process produces a mineral raw material with appropriate characteristics of a commercial product, which it obtained in the process of enrichment. This is a long-term stage. The last stage is a closure of the mine and reclamation of the area where the exploitation was conducted.

Given the above, it is noted that the life cycle of the geological-mining project is identified directly with the life cycle of the mine (Fig. 1). A mine's life cycle includes the following stages [22]:

- prospecting and exploration,
- development,

extraction,

• closure/reclamation.

It is worth noting, that it may be difficult to distinguish the individual stages of economic activity as some processes may overlap or occur in parallel during certain periods.

Exploration works consist in finding and documenting mineral deposits; in particular, they include:

- analysis of historical geological data,
- topographical analyses,
- geological analyses,
- geochemical and geophysical analyses,
- exploratory drilling,
- sampling.

Such exploration works can only be performed after the relevant rights and licenses have been obtained.

Since as much as 95% of projects never go past the exploration stage and reach the deposit evaluation stage, exploration and identification of deposits bears the highest risk of failure. The relationship between the investment risk and the stage of a mining and geological project's life cycle is presented in Figure 2.

When analyzing the entire life cycle of a project, it is evident that the risk changes depending on the stage of its implementation (fig. 2). The initial stage, being mostly exploration, is characterized by a high risk of failure, demanding at the same time high investment assets, related to the necessity of relevant research and analyses. Investment outlays typical-



Fig. 4 Exploration expenditures on particular types of raw materials between 1975-2018 [36] Rys. 4. Wydatki eksploracyjne w zależności od rodzaju surowców w latach 1975-2018



Fig. 5. Changes in exploration expenditures in the four countries that represent the largest market for exploration [36] Rys. 5. Zmiany w wydatkach na eksplorację na przykładzie czterech krajów reprezentujących największe rynki eksploracyjne

ly amount to about a few percent of the value of the whole project (approx. 10-15%). The highest level of risk out of all project stages is due to the exploration works undertaken during this stage, including the drilling of exploratory wells, which does not always result in a deposit being discovered. In practice, one can never be certain that such works will lead to the discovery of commercial deposits. As the works on the exploration and the development of the deposit progress, the business risk decreases, although, in fact, it accompanies the investor until the end of the operation of the project.

Then, for projects that go further to the assessment stage of the deposit, the risk decreases significantly. The lowest risk occurs at the stage of the mine construction, the exploitation and the enrichment, i.e. once all parameters are known, the knowledge of the mineral is high enough and appropriate research and analysis have been carried out. Potential investors and capital providers pay attention to financial aspects, but above all, to technical or technological data concerning geological and mining information, the most of which occur, as mentioned, at the exploration stage. The decisions to start the investments in exploration, development and subsequent extraction of minerals from the deposit require a large initial capital commitment, while the economic benefits of the project are usually generated after a few or more years from the discovery of the deposit. Therefore, it is the characteristics of the deposit (the rarity of occurrence, the natural limitation, the lack of a possibility of estimating them unequivocally) that determine the financial success of the investor. The size of the deposit and resources is the basic condition for investment activity in mining. And the geological conditions of the occurrence of the mineral (the form of the deposit, the size of resources and the quality of the mineral) and the possibilities of its extraction determine the profitability of this investment. The deposits located close to the surface, with large resources and large thickness, are more economical than the small ones with a complicated structure, located much deeper.

3.2. Junior mines as a special purpose vehicle dealing with exploration works

Global consolidation of the mining industry (a global process of taking over and merging) which occurred after the first decade of the 21st century created more concentrated and limited mining market. Big companies using horizontal diversification model with diversified production and geographical location, identified with individual business segments within a specific business model started to dominate the market. (Figure 3)

The changes made most often through processes of merging and taking over led to shaping the specific market structure of mining companies in which one can distinguish three types of mining companies:

- senior mines,
- medium mines,
- junior mines.

The classification border between the classes of individual companies is blurred and the criteria for the division are different. For example, M. Dougherty uses the size of its assets as a classification criterion, i.e. senior mines would be mining companies with assets exceeding \$3 billion, medium mines



Fig. 6. Increasing the share of junior mines in global exploration [36] Rys. 6. Wzrost udziału junior mines w eksploracji na świecie



Fig. 7. Mine development stages and traditional sources of funding [32] Rys. 7. Fazy rozwoju projektu geologiczno- górniczego a tradycyjne źródła finansowania

between \$1 billion and \$3 billion, and junior mines below \$1 billion [28]. D. Cranstoun, on the other hand, distributes the classes by a source of income assuming that: seniors would generate revenues mainly from the extraction and sale of minerals, juniors would depend primarily on effective processes of exploration and sale of documented deposits without production, and the mediums would generate revenues in a complementary manner from both sources [18].

In the light of the cited classifications, it can be concluded that the structure of the mining market has been determined by the revenue generated but also by the specialization of works within the life cycle of deposits identified as geological-mining projects.

The increase in exploration expenditures over the years has become a necessity for extending the life of mining operations but also for increasing of future mining. (Figure 4) The figure shows that the successive increase in exploration expenditures had its highest value in 2012, and the value of exploration expenditures was approximately \$34.9 billion. As for the type of raw materials that absorbed the highest capitals at the exploration stage, it must be admitted that gold is invariably the leader. Base metals such as copper, zinc, lead or aluminium also have a significant share. In the last two years, i.e. 2018-2020, according to the PwC report, we can observe a transfer of high exploratory intensity to lithium and cobalt, which are necessary for new technologies very often related to the broadly understood electromobility.

As far as the countries with the largest exploration expenditures are concerned, they can actually be considered to be the largest in countries where regulations encourage this type of activity and at the same time where exploration companies can count on raising capital for such activity. Figure 5 displays the domination of four countries - Canada, Australia, USA and China.

Most of the investment expenditures made in the exploration works were made by junior mines companies. Figure 6 shows the share of exploration companies in the total global exploration effort; this share has been systematically increasing since the 1980s. In the last decade, more than 65% of all discoveries of new deposits were made by junior mines.

The rapid growth of junior mines was caused by specialization and the desire to separate the risks of existing mining businesses from exploration. The transfer of risk to special purpose companies has become effective for the largest mining concerns. Due to their specificity, junior mines companies need to finance their significant investment expenditures, which is why they participate in the capital market, where they try to obtain the necessary funds by issuing shares, most often



Fig. 8. Level of financing of juniors mines with equity and foreign capital in 2015-2018 [20] Rys. 8. Poziom finansowania spółek typu juniors przy wykorzystaniu kapitału własnego i długu

in alternative markets. The largest and most effective markets for such companies are found on the London, Toronto and Sydney stock exchanges. At the same time, the valuations of junior mines on the stock exchanges are generally low for the mineral sector, and their appreciation is conditioned by information about the mineral potential of the sought-after areas and the progress of projects" [30]. The implementation of projects by these companies or, more precisely, the possibility of finding economically viable extraction resources is significantly limited. Therefore, investments in these companies are subject to high risk. The risk also results from possible manipulation of information disclosed by mining companies [31]

4. Discussion

In the light of the presented models for the realization of exploration works, this chapter presents the types of funding and trends in the financing of exploration works carried out by junior mines.

Exploration works as the first stages in the implementation of projects generate expenses and potential revenues (or possibly profits) appear only in the operational stage related to the operation of the project. A drawing showing the generated assets, cash flow and financing sources at each stage of the life cycle is presented below.

As Figure 7 shows, the sources of funding in the exploration stage basically focus on equity only, which can come from the owners' contributions as well as form the issuance of shares on the capital markets. It is only at the stage of both technical and economic feasibility studies that it is possible to raise foreign capital and debt financing. The consequence of the presented trends and their conclusions is that junior mines dealing with exploration works have to raise equity for their activities, looking for opportunities to enter capital markets and distribute shares to potential owners. The funding structure for the individual life cycle phases of mining companies (Figure 8) in the years 2015 to 2018.

Figure 8 confirms the share of foreign capital in the financing of geological-mining projects with an increase in their advancement and a simultaneous reduction of investment risk. foreign capital financing at individual stages of the life cycle. In the case of juniors companies, which are mainly interested in the first stage (exploration), equity financing exceeds 90% (except for 2016, when equity financing was at the level of approximately 74%).

Within the framework of stock exchanges, these companies may issue shares on the capital markets, and in particular on the so-called alternative markets. [30]. The choice of such markets for juniors companies is due to the fact that they do not meet the requirements to enter the main market.

The biggest quotation markets for juniors companies in the mineral sector are:

- Toronto Stock Exchange (TSX) in Canada, the TSXV alternative market.
- Australian Securities Exchange (ASX) in Australia,
- London Stock Exchange (LSE) in England, AIM alternative exchange

The location of stock exchanges in these countries is primarily due to the predictable and stable regulatory environment and the proximity of some areas rich in minerals, i.e.: the proximity of London to Africa, Canada to all the Americas and Australia to Asia, Africa and Australia. These countries have attracted mining companies to their financial market by providing opportunities to raise capital and develop them in mining and related industries.



Rys. 9. Finansowanie prac eksploracyjnych w Kanadzie

According to J. Bhandari, Canada has the highest number of junior mines listed on the stock exchange [13]. Thus, the Toronto Stock Exchange Venture (TSXV), as an alternative market, are leaders in raising finances for exploration companies. Many of the companies listed on these stock exchanges do not come from Canada, but they take advantage of the favourable regulatory and market conditions offered by Canada to obtain financing. It is about the stability of not only legal regulations but also investment incentives, created by the state to purchase shares of junior mines companies by potential shareholders. This includes several editions of the "Flow through shares" program (Figure 9)

In turn, by analyzing the Australian market in the context of exploration and potential incentives created by the state, it is also possible to identify programs of which two were the most significant:

• Plan for Accelerating Exploration (PACE) for the South Australia region, under which over 40 million US dollars were spent in 2004-2015;

• Exploration Incentives Scheme (EIS) supporting the Western Australia region, within which approximately 100 million US dollars have been spent between 2009-2017.

In each of them, there has been an intensification of searching and strengthening of the sector of Australian junior mines operating on the market.

In recent years, specialized private equity funds have also been very expansive in funding exploration works, complementing traditional sources of capital from the capital market. These funds are an alternative form of financing and are targeted at investments in the early stages of geological-mining projects. The most active ones include Orion Mine Finance, Resource Capital Funds, Taurus or Greenstone Resources.

Private equity offers funding to junior mines in exchange for minority shares in projects. They are also given influence on management and operational decisions to increase their profitability in the context of final sales.

The funds have also recently recognized opportunities to lengthen the value chain when financing projects and have combined investing in the exploration of new deposits with opportunities to secure priority in debt financing at subsequent stages of geological-mining activities; e.g. Orion obtained rights for debt financing for the Curraghinalt project, just like Greenstone Resources in the case of two copper projects, Coro and Excelsior [34].

Creating opportunities to earn money by offering different types of financial products for private equity funds at different stages of projects seems to be beneficial for the mining market and offers an opportunity to attract similar types of financing on a wider scale

5. Conclusions

Currently, mining companies operating on the market have to face challenges related to the general downturn, decrease in raw material prices, maintaining cost efficiency, and finally the need to implement new and innovative solutions to improve their geological and mining processes.

In the early stages of geological-mining activities, the identified exploration processes require financial expenditures, while incurring a very high investment risk, associated with the failure of exploration. In the light of the conditions and risk management, which determines the cost of raising the necessary capital, the exploration works are mostly carried out by junior mines special purpose companies. They usually raise equity through share issues on alternative markets, the largest of which operate in Toronto TSXV, London AIM and Sydney ASX. However, equity does not fill the existing financing gap at the earliest. Recently there has also been an observable activity of equity private funds, which offer funding to exploration companies. Having minority shareholding, they gain influence on the implementation of geological-mining projects, bringing them to the stage where a project with documented deposit can be resold. Nevertheless, some of the funds have seen opportunities of extension of licenses to earn money by ensuring the provision of capital at further stages of project development. Such an extension of the value chain for financial products owned by private equity funds is economically justified, but on the other hand, it should also have a positive impact on the development of the mining market.

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Źródła finansowania prac eksploracyjnych w świetle ryzyka związanego z ich realizacją

W artykule przedstawiono przegląd uwarunkowań prac poszukiwawczych oraz określenie roli spółek typu junior mines w tych procesach. Junior mines, jako spółki celowe, koncentrują się na etapach poszukiwania i dokumentowania złóż, nie wchodząc w fazę operacyjną związaną z eksploatacją. Ze względu na swój charakter, podmioty te finansują swoją działalność kapitałem własnym w formie emisji akcji na rynkach kapitałowych, kierując swoje papiery wartościowe do inwestorów akceptujących wysoki poziom ryzyka. Zidentyfikowano największe giełdy, na których spółki eksploracyjne pozyskują źródła finansowania oraz przedstawiono aktualne tendencje pozyskiwania kapitału, dotyczące zaangażowania funduszy private equity.

Słowa kluczowe: górnictwo, eksploracja, spółki junior mines, finansowanie



Level of Accumulated Depreciation of Energy Companies' Assets

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Abstract

The paper presents the degree of accumulated depreciation of fixed assets in Polish energy companies against the background of global energy companies. The coal-fired energy units used in the Polish energy industry are outdated and require replacement. In the course of the energy transformation, they will be replaced with energy from renewable sources, natural gas and nuclear fuel. The transformation of the energy sector will allow the achievement of climate and environmental goals. Depreciation charged to expense is an internal source of financing for processes of restoration of the production capacity. However, the Accounting Act and the Income Tax Act provide for different methods of calculating depreciation, which means that not all depreciation is tax-deductible and that it does not reduce the tax base. Reducing the discrepancies in legal solutions regarding the calculation of depreciation in companies may stimulate the implementation of the processes of energy transformation.

Keywords: depreciation, average depreciation rate, accumulated depreciation of assets

Introduction

Fixed assets used by a given entity in the course of its business activity are subject to wear and tear over time. The entity must earmark funds for their replacement. This is done by systematically charging the depreciable amount to expense in the entity's profit and loss account/income statement. Depreciation becomes an expense but does not entail immediate expenditure so as to replace a given asset. Thanks to depreciation, the company can recover in instalments the capital it tied up in its assets. This capital can then be used to finance current investments or to service debt incurred to finance investment. Therefore, depreciation cannot be considered in isolation from the entirety of the company's activity. By being an expense for the company, depreciation can be used to control the company's profit/loss. An increase in the costs allows the company to post a lower net profit divided by shareholders during their General Meeting between a part consumed by themselves and a part retained to fund development. Depreciation can also be used as an instrument facilitating the control of the level of tax liabilities and the size of the financial surplus in specific periods. It is used to service debt, hence it is of interest to the providers of external capital.

The paper aims to assess the level of accumulated depreciation in energy companies from the angle of the need to replace their coal-based production capacity with a capacity based on renewable energy sources. The working hypothesis guiding this research holds that the level of fixed asset depreciation in Polish energy companies is higher than in global energy companies, which will accelerate the transformation of the Polish energy sector.

Depreciation as a reflection of the degree of assets' wear and tear

Fixed assets used in the pursuit of business activity are subject to systematic degradation, which reduces their value in use or exchange value. Pertinent literature recognises various reasons for a decline in assets' value in use. The decline may be gradual over an asset's useful life, or sudden as a result of excessive dynamic workload of a thermal, mechanical or chemical nature, or it may result from a failure. The physical degradation of fixed assets occurs as a result of their use in production, service and other economic activity processes. According to (Martyniuk, 2008), the relationship between the scale and rate of this wear and tear results from an interplay of:

- physical and chemical properties of the fixed assets concerned,
- the age of the fixed assets,
- intensity and conditions of use,
- frequency, method and scope of repairs.

An asset may be physically fit for uninterrupted use, but its degradation due to economic influences may rule out such exploitation. The obsolescence of fixed assets is caused by technical and technological progress leading to the emergence of assets with better technical and operational parameters. These new assets are superior and make it possible to increase labour productivity and manufacture products better and more cost effectively. The obsolescence of fixed assets results in the loss of their value in use before they reach the end of their physical life.

The wear and tear of fixed assets is reflected in accounting records. Accounting recognises two meanings of wear and tear of a fixed asset (Szczypa, 2011):

- accumulated depreciation showing the decrease in the initial value of the fixed asset,
- depreciation, which is an element of a product's manufacturing costs for the company.

Depreciation spreads the value of a depreciable fixed asset over its useful life and charges it to the company's expenses in order to recoup the expense incurred to obtain it, thereby creating a fund for its replacement after its life ends. The Tab. 1. Degree of accumulated depreciation of tangible fixed assets and intangible assets in selected energy companies in 2015-2019. Source: own calculations based on information in the balance sheets of the analysed companies obtained from a Reuters database.

W latach 2015-2019							
Name of company	2015	2016	2017	2018	2019		
Enea	35.18	35.97	35.63	36.89	38.97		
Energa	33.49	37.34	38.92	38.91	40.23		
PGE	45.25	44.83	42.40	43.01	49.14		
Tauron Polska Energia	37.86	39.66	40.30	41.60	42.34		
Iberdrola	38.65	38.72	39.65	-	39.45		
NextEra Energy Inc.	23.58	23.10	22.74	23.58	23.36		

43.53

2<u>7.65</u>

33.41

45.98

29.84

33.52

Tab. 1. Stopień umorzenia rzeczowych składników majątku trwałego i wartości niematerialnych i prawnych w wybranych spółkach energetycznych w latach 2015-2019

initial value of the fixed asset is the basis for calculating depreciation. The initial value is its purchase price, the cost of its manufacturing or construction if the fixed asset is made in-house, fair (market) value if the fixed asset is received as an inheritance, donation or otherwise on a free-of-charge basis. In the case of leasing, its initial value is stated in the leasing contract (Aleszczuk, 2012). The initial value of fixed assets may change in the course of their exploitation as a result of their improvement or modernisation as well as due to the official revaluation of fixed assets.

The method of calculating depreciation amounts charged to expense is regulated by provisions of the Accounting Act and the Corporate Income Tax Act (CIT). The Accounting Act allows economic entities to both autonomously determine depreciation rates and to choose the depreciation method. Moreover, it indicates that in selecting the depreciation rate and method, the economic useful life of the fixed asset should be taken into account as the first priority. Pursuant to article 32 of the Accounting Act, the economic useful life is determined in particular by:

- the number of shifts worked by the fixed asset;
- the pace of technological and economic progress;
- fixed asset's productivity measured in terms of the number of hours worked or the number of manufactured units or any other appropriate measure;
- legal or other restrictions on the use of the fixed asset;
- the net selling price of a significant remainder of the fixed asset anticipated at liquidation.

"In the part relating to depreciation, the Corporate Income Tax Act sets out the principles underpinning the determination of depreciation for the purposes of calculating income tax, and it does so in a more restrictive way than the Accounting Act. The lawmaker provided for the possibility for companies of using various depreciation methods for tax deductible costs" (Cygańska, 2014). The provisions of this act show that entrepreneurs can choose from among three depreciation methods (Iwin-Garzyńska, 2012):

a) one-off

SSE PLC

Valero Energy Corp

Xcel Energy Inc

b) linear, using standard, increased or reduced depreciation rates as specified in the Schedule to the Act,c) linear, using individualised depreciation rates,d) declining balance

The one-off depreciation method involves one-time recognition of the value of the acquired fixed asset as a tax deductible cost. As a rule, the right to one-off depreciation is granted to small taxpayers or taxpayers starting business activity and is applied to fixed assets from group 3-8 of the Classification of Fixed Assets (KST) (other than passenger cars) in the tax year in which these assets are recorded in the register of fixed and intangible assets, up to a value not exceeding the equivalent of the limit on the aggregate value of such depreciation in the given year. In 2021, the deductible amount totals 50 000 euro. (Kuchta, 2021). The linear method means depreciation made in equal monthly or quarterly instalments. It also is the primary depreciation method for tax purposes. The depreciation is made from the first day of the month following the month in which the fixed asset is recorded in the register. With regard to this method, the lawmaker allows the possibility for companies to apply higher and lower depreciation rates relative to the standard rates included in Schedule 1 to the Act. Moreover, in certain cases it is possible to use individualised depreciation rates. Increased depreciation rates can apply to:

49.38

31.32

34.50

49.66

32.08

32.85

47.66

32.94

- buildings and structures used in: demanding conditions – coefficients of 1.2 or less can be used, and poor conditions – coefficients of 1.4 or less can be used;
- machines, equipment and means of transport, except for marine vessels, used more intensively relative to average conditions or conditions requiring exceptional technical efficiency – coefficients of 1.4 or less can be used for such periods;
- machines and equipment from groups 4-6 and 8 (KŚT), based on separate regulations, subject to rapid technological progress – coefficients of 2.0 or less can be used.

The company has the option to lower the depreciation rate specified in the schedule to the act, however, as a result, the income tax base rises. The possibility to increase or lower the depreciation rates is an expression of the principle of flexibility of the tax regime. It is one of the basic principles underlying the construction of a common consolidated tax base and the concept of harmonisation of income taxes across the European Union. On the other hand, solutions are being sought to support standardisation and objectification of tax income determination, and consequently easier comparison of tax burdens.

The current system of fixed asset depreciation enables companies to apply individual depreciation rates for improved or second-hand components of fixed assets. The rates for these assets are set by the company itself, but the depreciation period resulting from the rate it applies must not be Tab. 2. Age structure of Poland's distribution network in 2019, in percentage. Source: Forum Energii, M. Janik Sieć dystrybucji prądu należy utkać od nowa Rzeczpospolita, Ekonomia & rynek 15 July 2019, p. A20

Tab. 2. Struktura wieku sieci dystrybucyjnej w Polsce w 2019 roku, w proc. Źródło: Forum Energii, M. Janik Sieć dystrybucji prądu należy utkać od nowa Rzeczpospolita, Ekonomia & rynek 15 July 2019, p. A20

Type of line	Over 40 years	25 – 40 years	10-25 years	Under 10 years
HV overhead lines	42	34	15	9
HV cable lines	3	0	17	80
HV/MV stations	30	33	20	17
HV/MV transformers	19	33	19	29
MV overhead lines	37	39	17	7
MV cable lines	16	24	28	31
MV/LV stations	28	32	22	19
MV/LV transformers	15	29	25	31
Overhead lines	31	35	21	13
LV cable lines	13	25	31	31

shorter than that specified in the pertinent act in respect of the individual groups of fixed assets. Apart from the linear method, Polish tax regime permits the use of the accelerated, declining balance method. It assumes decreasing depreciation charges resulting from the declining usefulness of the fixed asset over the course of time of use. This is due to the assumption that the fixed asset ages over time, which means that it is less productive and requires increasingly frequent maintenance and repairs. The amount of annual depreciation in the first years of use is higher than the annual depreciation under the linear method and in subsequent years it becomes lower and lower. Accelerated depreciation of fixed assets in the first years of its operation stimulates the company to use them intensively when they are still new and technically efficient.

The declining balance method is considered to be a form of tax preference, as increased depreciation reduces the company's taxable income and, consequently, also its income tax payable. Accelerated depreciation of a declining balance nature may be applied to machinery and equipment classified as groups 3-6 and 8 according to the Central Statistical Office classification of fixed assets and to means of transport other than passenger cars. Pursuant to the provisions of the Act, in the first year of exploitation of the fixed asset, the company uses the depreciation rates stipulated in the list, increased by a factor of 2 or less. The factor of increase in the depreciation rate used under the declining balance method may not exceed 3, but only in the case of fixed assets that may be depreciated under this method. The above holds for funds in a plant located in a commune with a particular risk of high structural unemployment, or in a commune threatened by recession and social degradation. In the subsequent tax years, depreciation is made from the net (present) value determined at the beginning of subsequent years, i.e. from the gross initial value less depreciation charges to date. However, starting from the tax year in which the annual depreciation amount so determined would be lower than the annual depreciation amount calculated using the straight-line method (without the adjustment factor), the company makes further depreciation using the linear method. The regulations on the declining balance method also contain preferential provisions for start-up entrepreneurs and for 'small taxpayers'. These entrepreneurs can use depreciation including one-off depreciation of up to 100% of the initial value of the fixed asset in the first tax year (Article 16k of the Act). This applies to fixed assets from groups 3-8 (KŚT), including machinery, equipment and means of transport other than passenger cars.

Research method

Financial statements of listed energy companies were sourced from a Reuters database. Based on information in the statements, the ratios showing the degree of depreciation of tangible fixed assets and intangible assets as well as the average annual depreciation rate for these assets were calculated. The degree of asset's accumulated depreciation was calculated as the ratio of the aggregate depreciation to the gross value of depreciated assets at the end of the calculation period. The average annual depreciation rates for these assets are the ratio of the annual depreciation to the gross value of the depreciated assets. At PGE, the globally reported depreciation level also included impairment charges. In 2016-2019, large write-off were made on account of revaluation of assets used, which upset the comparability of the analysed values. In order to ensure the comparability of data, the amount was verified and the average annual depreciation ratio was calculated taking into account only the accrued depreciation.

It should be added that the level of the calculated ratios was influenced by changes in accounting principles and the implementation of new global financial reporting standards into accounting practice. The biggest changes were caused by the implementation of IFRS 16 Leases in 1 January 2019. The new IFRS 16 changed the rules for recognising contracts defined as leases. The main change involves the departure from the split between financial lease and operating lease for the lessee. All lease contracts came to be treated as finance leases and were recognised in the balance sheet, while prior to the implementation of the standard, the property used under operating lease contracts was not recognised in the balance sheet. In addition, the value of lease, rental, lending and similar agreements came to be assessed. These values were discounted and their current value was incorporated into the balance sheet.

Degree of accumulated depreciation of fixed assets in energy companies

Table 1 shows the degree of accumulated depreciation of tangible fixed assets and intangible assets in energy companies. The figures in the table indicate a relatively high level of accumulated asset depreciation in Polish energy companies – it ranges between 35 and 45% of their production capacity. The companies are burdened with outdated production capacities in which coal is the energy carrier. Over 70% of energy generating units are over 30 years old and they will have to be decommissioned in the next 20 not only because of the climate policy, but mainly because of their obsolescence

Tab. 3. Average annual depreciation rate for tangible fixed assets and intangible assets in selected energy companies in 2015-2019. Source: own calculations based on the balance sheet data for analysed companies sourced from a Reuters database

Tab. 3. Średnioroczna stopa amortyzacji rzeczowych składników majątku trwałego i wartości niematerialnych i prawnych w wybranych spółkach energetycznych w latach 2015-2019

Company name	2015	2016	2017	2018	2019
Enea	2.97	3.81	3.70	4.36	4.29
Energa	4.58	4.46	4.33	4.03	4.20
PGE	4.87	4.15	3.94	3.52	3.41
	13.72*				9.46*
Tauron Polska Energia	4.37	3.65	-	3.52	3.44
Iberdrola	3.28	2.84	4.11	-	3.37
NextEra Energy Inc.	3.99	3.94	2.82	4.49	4.16
SSE PLC	7.09	4.70	4.23	3.05	3.92
Valero Energy Corp.	4.99	5.02	4.96	4.87	4.94
Xcel Energy Inc.	2.74	2.99	3.25	3.36	3.37

ncluding revaluation write-offs on fixed assets, which are reported in the cash flow statement together with preciation.

(Boroń, 2021). The programme of rebuilding the energy sector assumes the elimination of these capacities and a transition to alternative eco-friendly energy sources.

The balance sheets of SSE PLC were as of 31 March, hence the figures for each year cover a period of 1 April-31 March of the following year.

A degree of asset depreciation similar to that of Polish companies is reported by the Spanish company Iberdrola and the British-Irish company SSE PLC. The American energy company NextEra Energy Inc. which produces energy from alternative sources has the lowest level of asset depreciation consistently staying at below 25%. Notably, accumulated depreciation levels of assets were systematically rising across all Polish energy companies. In PGE they exceeded 49% in 2019. This year, the company reported exceptionally high impairment losses on assets - PLN 7 518 million (Note 7.2.1. to the statements). Coupled with depreciation, these 2019 write-offs amounted to PLN 11 417 million, while PGE's depreciation of PLN 3 985 million was comparable to that of the previous year when it totalled PLN 3 893 million. Recognition of such high revaluation write-offs resulted in a loss of PLN 3 928 million. In 2018, the company generated PLN 1 511 million in profit.

Apart from outdated production capacities, Polish energy companies are also saddled with an outdated power grid. Only one in five kilometres of the network is less than 25 years old. An overhead line-based power grid predominates. Cables account for approximately 20% of the power grid. The increasingly extreme weather phenomena (e.g. heavy snowfall in January 2021) have an adverse effect on power lines, causing them to break. Most of these networks at the transformer station level require investments in safety instrumentations solutions. The age structure of Poland's energy distribution network is presented in Table 2.

42% of high-voltage overhead lines are over 40 years old and 76% are over 25 years old, and a further 63% of HV and MV stations are over 25 years old. Only 24% of MV overhead lines are less than 25 years old. M. Janik (2019, p. A20) contends that the state of the national transmission system is similar to that of such European countries as Germany, France and Austria. However, the pace of planned modernisation in these countries is much higher than in Poland. Industry 4.0 requirements demand rapid network modernisation. It becomes necessary to implement intelligent systems controlling network parameters, to build insulated lines, use modern energy storage technologies, which may be a reasonable alternative to building new lines. The development of electromobility and the connection to the grid of an ever greater number of dispersed energy sources also require investment in the distribution network. It is necessary to expand the power grid in the north of the country, including to connect offshore wind farms and distribute energy around the country.

Changes in the principles underlying calculation of depreciation had an impact on the increased level of depreciation and the accumulated depreciation of assets in Polish energy companies. The companies analysed different types of contracts to see whether a given contract includes a lease. Pursuant to the definition of IFRS 16, leasing contracts in energy companies include:

- perpetual usufruct of land both purchased and received in kind, or received free of charge on the basis of an administrative decision,
- land and transmission easements,
- lease and hire agreements, etc. related to the location of line and technical infrastructure (heating nodes, transformers),
- hire and lease agreements, etc. of office premises,
- hire and lease agreements etc. of buildings, structures and technical equipment.

The value of assets was affected the most by the recognition of perpetual usufruct of land and land hire/lease agreements, which, before the entry into force of IFRS 16, were recognized as operating leases. Not all contracts were treated as solutions subject to the provisions of IFRS 16, though. For example, following careful analysis, PGE concluded that the scope of IFRS 16 does not cover contracts for the occupation of a road lane for the purposes of placing energy infrastructure, for which a significant replacement right was found to apply, or contracts of lease of links/optical fibres/power cable ducts. In the case of easement contracts for the laying of overhead infrastructure, the non-leasing component (overhead line) constitutes the dominant element of such contracts. The share of the leasing component (pole/pylon) is immaterial. Decisions regarding the occupation of a road lane generally fall within the scope of the provisions of a definition of a lease. However, within the PGE Capital Group, wherever there are cases of the road administrator using the legally mandated right to request relocation of infrastructure laid along the road lane, its companies do not enjoy the full right to manage the use of the identified asset. In this case, the contracts do not satisfy the provisions of the definition of a lease. In the case of lease agreements for links/optical fibres/power cable ducts, the Group does not use most of the production capacity of the asset. Consequently, in accordance with IFRS 16 the asset does not fulfil the criteria of an identified asset, and the above-mentioned contracts (e.g. a contract for the lease of capacity on a fibre optic line) do not fall within the scope of the definition of a lease. On the other hand, in the case of easement agreements for the laying of overhead infrastructure, the dominant element of the agreement is constituted by the non-leasing component (overhead line). The share of the leasing component (pole/pylon) is immaterial. Easement agreements generally meet the definition of lease covered by IFRS 16, however, due to their insignificant impact on the value of assets, they were recognised as lease in accordance with IFRS 16 (PGE Consolidated Report, p. 38).

Average rates of asset depreciation

The possibility of replacing a company's assets is determined by the level of the selected depreciation rates. These show the intensity of assets' use, which affects the level of their productivity. Table 3 shows the average depreciation rates in energy companies – these were calculated as a ratio of accrued annual depreciation to the gross value of depreciated assets. They are relatively low, ranging between 2.5 and 5.0% of the gross value of the depreciated fixed assets. This is due to the structure of the fixed assets held, dominated by buildings, structures and electricity transmission networks that have a very long useful life.

The balance sheets of SSE PLC were as at 31 March, hence the figures for each year cover a period of 1 April - 31 March of the following year.

During the study period, the average depreciation rates increased in three companies (Enea, NextEra, Xcel Energy Inc.), while Tauron, SSEplc and PGE reported a decrease caused by the termination of depreciation of certain assets and a low level of new investments.

However, the investment needs of Polish energy companies are much greater than those of global companies. Poland's coal-powered electricity production increases CO, emissions. Under Poland's energy policy until 2040, in 2040, coal is to generate 11-28% of electricity depending on CO_2 prices. There are plans involving the construction of a nuclear power plant and an increase in energy production from renewable sources, including from wind farms, photovoltaics, biogas and hydrogen. This means that huge capital outlays are required to transform the energy sector in Poland and eliminate obsolete coal-fired energy units and transmission networks.

Conclusions

In summary, it should be emphasised that the hypothesis formulated in the introduction to the paper has been confirmed. The degree of accumulated depreciation of fixed assets in Polish energy companies is higher than the same in global energy companies. Obsolete coal-based production capacities predominate. The energy transmission network is similarly outdated. In the coming years, Poland will have to undergo an energy transformation involving not only the elimination of obsolete coal-fired power units, but also adjustment to EU requirements for climate and environmental protection. In December 2020, the European Council reached agreement on increased greenhouse gas emissions reduction target from 40% to 55% by 2030. In the new financial perspective, Poland will receive PLN 130 billion in the form of grants. More than one third of this amount should be allocated to financing environmental and climate projects. The most important projects will include: development of renewable energy sources, energy efficiency, digitisation of the energy sector and clean heat (heating networks and heating). Projects in the area of heat engineering should be a priority, as it is one of the important operating segments of Polish energy companies. Energy companies operate coal-fired heating plants, which were built in the seventies and eighties, and are now outdated. Additionally, CO₂ emissions charges are increasing, which will accelerate transformation in the heating industry. In the course of transformation of the Polish energy and heating industry, the country's energy security should be the underlying factor of the decision-making process. The development of energy generation based on alternative energy sources will require the implementation of flexible capacities around natural gas. It should be noted that investments in the energy sector will stimulate the development of the Polish economy and accelerate recovery from the economic crisis.

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Poziom skumulowanej amortyzacji majątku przedsiębiorstw energetycznych

W artykule zaprezentowany został stopień umorzenia środków trwałych polskich spółek energetycznych na tle światowych koncernów energetycznych. Wykorzystywane w polskiej energetyce bloki węglowe są przestarzałe i wymagają wymiany. W wyniku transformacji energetycznej będą one zastępowane energią z odnawialnych źródeł, gazu i paliwa jądrowego.

Transformacja energetyki pozwoli na realizację celów w obszarze klimatu i środowiska. Naliczana w ciężar kosztów amortyzacja stanowi wewnętrzne źródło finansowania procesów odtwarzania mocy produkcyjnych. Jednak przepisy ustawy o rachunkowości i ustawy o podatku dochodowym różnicują sposób naliczania amortyzacji co powoduje że nie zawsze cała amortyzacja stanowi koszt uzyskania przychodu i nie pomniejsza podstawy opodatkowania. Ograniczenie rozbieżności w rozwiązaniach prawnych dotyczących naliczania w przedsiębiorstwach amortyzacji może wpłynąć stymulująco na realizację procesów transformacji energetycznej.

Słowa kluczowe: amortyzacja, średnia stopa amortyzacji, skumulowane umorzenie majątku trwałego



Liquidity Measurement Problems in Mining Companies

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Abstract

The ability to manage liquidity is important in any economic conditions. It assumes unique importance during a downturn and depends on management having reliable information on the company's liquidity level. Static liquidity ratios do not provide such reliable information. Their high values result from high inventory levels of extracted raw materials and is not tantamount to excess liquidity. Additional information is offered by the cash cycle and its constituents – Days Inventory Outstanding, Accounts Receivable Days and Accounts Payable Days. Long cash cycles signal a shorter deferral of settlement of suppliers' bills and a lower liquidity level. To maintain liquidity, companies must maintain higher cash balances in their accounts. Short cycles, on the other hand, may result from late payment of invoices, which is reflected in long Accounts Payable Days. Some coal companies have very long Accounts Payable Days and negative cash conversion cycles. This means that some of their non-current assets are financed out of current liabilities.

Keywords: liquidity, liquidity ratios, cash cycle

Introduction

Company's ability to maintain liquidity is a basic precondition for ensuring continuity of its operations. Business entities that have lost liquidity tend to collapse more often than those that generate losses from time to time. If the entity is not able to meet its obligations in a timely manner, this disturbs the broader financial equilibrium and contributes to the emergence of payment gridlock. Loss of liquidity means that the company has lost its ability to pay maturing current liabilities on time because of its inability to cover operating and financial expenses out of the revenues generated during the current period or out of previously accumulated funds. Companies' experiences during the crisis in 2020 produced stronger interest on the part of managers and the state in methods ensuring liquidity and reducing the risk of running a business. Rational decisions underpinning liquidity management are a prerequisite for companies' survival and development. However, they must be based on reliable information and correct liquidity measurement.

The paper aims to show liquidity measurement problems in coal companies resulting from the specificity of their operating activities. The analysis aims at verifying the hypothesis that the level of static liquidity ratios is determined by industry specificity and does not correctly reflect the company's liquidity.

The Essence of Liquidity

Authors define the concept of liquidity in various ways and give it a multidimensional meaning. Liquidity can be viewed in terms of assets, capital and assets and cash flow. The first aspect focuses on the ease with which the company can convert its assets into cash at the shortest possible notice and without any or with only a minor loss of value (Wędzki 2003, p. 33). The capital and assets aspect expresses the company's ability to settle its current liabilities within the prescribed period (Sierpińska, Jachna 2009, p. 79). On the other hand, the cash flow aspect indicates that the company maintains liquidity if the expenses needed to cover amounts due can be settled in a timely manner from current cash inflows. Liquidity is the company's ability to generate cash flows that allow it to meet its maturing current liabilities and cover unexpected cash expenses. Wędzki (2003, p. 33) points out two basic aspects of liquidity: the purpose of money spending and the source of its origin. Unexpected expenses may be associated with the purchase of raw materials and goods at bargain prices, the need to pay fines or higher than expected financial costs caused by an increase in interest rates.

Liquidity must not be confused with solvency. In the broad sense of the word, liquidity means the ability to settle current liabilities on time, while solvency is the ability to cover total debts out of the assets held. Solvency is sometimes defined as long-term liquidity (Sierpińska and Jachna 2009, p. 145). D. Wędzki distinguishes two types of solvency: shortterm and long-term. He argues that short-term solvency is the possession by the company of assets which can be easily tuned into cash and reserves of cash and securities, whereas longterm solvency is defined as the long-term surplus of the company's assets over the liabilities used to finance them. There is no unanimity in foreign literature in respect of the concept of solvency. D. E. Kieso and J. J. Weygandt (1992, p. 209) define solvency as the company's ability to pay its debts when they are due. In turn, C. J. Bond [1993, p. 492] does not define solvency, explaining the term "insolvent" instead. A debtor is insolvent when its total debt exceeds its total assets.

To maintain liquidity, the company sometimes runs into periodic excess liquidity. Excess liquidity means that the company holds funds that it is not able to use effectively. Keeping financial surpluses in the current account contributes to a decline in management efficiency because the interest accrued on such accounts is close to zero (Kwiecień, 2015, p. 41). Lack of liquidity and excess liquidity may both undermine profitability, market position and even lead to bankruptcy. To prevent this, the owners of the entity should maintain control over current and future liquidity levels, control cash flows and take appropriate steps to ensure financial equilibrium.

Liquidity Measurement

The concept of liquidity is inextricably linked with the methods of its measurement. The company's liquidity can be measured and assessed by looking at the state of current assets and current liabilities as of the financial statements date or cash flows generated by the company in the analysed period. Hence, pertinent literature presents static methods of liquidity measurement based on balance sheet data and dynamic ones based on cash flows. Liquidity metrics based on financial flows show what funds the company had at its disposal in a given period, what was their source of origin and how they were employed. In liquidity management, special importance is attached to cash flows from operating activities.

To measure liquidity statically, use is made of the current ratio, the quick ratio and the short-term investment ratio. The current ratio is the ratio of current assets to current liabilities. This ratio makes it possible to establish whether the assets from which the company will realise cash within one balance year will suffice to settle the liabilities due within the balance sheet year. Pertinent literature recommends varying values for this ratio. According to M. Sierpińska, T. Jachna (2009, p. 147), the ratio should range between 1.2-2.0, while W. Rogowski, M. Lipski (2014, p. 13) place it between 1.5-2.0 and J. Ostaszewski and T. Cicirko (2006, p. 182) narrow the range to 1.6-1.9.

The quick ratio shows the company's ability to cover current liabilities out of the sum of receivables realisable within 12 months and short-term investments. Pertinent literature puts the ratio in the range of 1.0-1.2 (Sierpińska, Jachna 2009, p. 147). Some authors argue that a rational level is 1.0, others range it between 0.9-1.0 (Ostaszewski, Cicirko 2006, p. 183). The short-term investment ratio is the ratio of shortterm investments to current liabilities. Pertinent literature puts the ratio should within the range of 0.1-02, which means that short-term investments should suffice to cover 10 to 20% of current liabilities. P. Szczepaniak (2014, p. 175) puts it at 0.2-0.3. The value of the figure depends largely on the financial strategy pursued by the management board. Both a shortage and excess of short-term investments are detrimental to the company and adversely affect its financial results.

If the calculated liquidity ratio falls short of the standard value, the company is believed to be likely to have difficulties with timely settlement of current liabilities. Contrariwise, when the value of the liquidity ratio is higher than the standard, it is assumed that there is excess liquidity. Such a normative approach to liquidity measurement is highly debatable. The value of the liquidity ratios is influenced by numerous factors beyond the management board's control and further reflects the specificity of the industry, economic situation, inflation and interest rates.

The assessment of the company's liquidity is the subject of extensive analyses, both domestically and abroad (Ashraf 2012, pp. 21-45), (Kirkham 2012, pp. 1-13), (Gowthami 2012, pp. 45-60). Pertinent literature concerned with the subject of economic and financial analysis features studies on the differences between the ratios and these are explicated by means of various liquidity determining factors. For example, research into the impact of company size on liquidity conducted by D. Zawadzka (2009) and G. Michalski (2005, pp. 55-65) shows that as the company grows, its liquidity ratios (both current and quick) mostly tend to decrease.

Liquidity assessment based on ratios of the level of current assets or their selected elements and current liabilities is not sufficient to unequivocally establish whether a decrease or increase in liquidity ratios reflects the company's actual liquidity. To calculate liquidity ratios use is made of the current assets and current liabilities as of the period for which the financial statements were compiled. In this way however, only the historical values of these assets and liabilities are included in the account. Static financial liquidity ratios disregard the time needed to convert current assets into cash, or the time specificity when current liabilities are being settled. The ratios measure the coverage of the company's future liabilities with the assets it has at its disposal during the current period. Moreover, the level of liquidity ratios may be the result of various manipulations, especially when they are used to assess management's performance.

To gain a reliable picture of the company's financial standing, the static liquidity assessment should be supplemented with additional liquidity metrics, which can partially eliminate these errors. A comprehensive approach to liquidity necessitates analysis of the duration of the cash cycle. This cycle is the sum of the Days Receivable and Days Inventory Outstanding less Days Payables Outstanding. Relevant literature states that determining the Days Payable Outstanding, shortterm debt on account of loans and borrowings and the issue of short-term debt securities should be disregarded, and only ad-hoc short-term debt should be included in the calculation. Regarding the cash cycle, the lower its value, the faster the company realises cash for the products it sold. A high value of the cash cycle implies that the company takes longer to realise cash and, consequently, the ratio may indicate liquidity problems. The longer the cash cycle, the more working capital the company must tie up to finance operating activities. This may lead to an increase in the average cost of capital and restrain the company's development. The average cost of capital may turn out to exceed the rate of return on investment that the company intends to make. Low liquidity ratios are associated with low cash cycles.

Liquidity Determinants

To determine the causes of changes in liquidity levels, the analyst should have a good understanding of liquidity determinants. These determinants can be systematised using various criteria. Pertinent literature most often mentions the extent criterion whereby the factors affecting liquidity can be divided into (Grabowska 2012, p. 20):

 microeconomic – the company's market position, pricing strategies, forms of settlements with suppliers, trade credit rules, management of net working capital, volatility of cash flows, implementation of investment projects exceeding a reasonably justifiable level, irregularities in current financial decisions. Microeconomic factors depend on the actions of individual economic entities. Tab. 1. Current and quick liquidity ratios in mining companies pursuing diversified activities, 2015-2019. Source: own calculations based on Ratios – Key Metrics retrieved from a Reuters database

Company	Ratio	2015	2016	2017	2018	2019
Anglo American PLC	Current Ratio	2.36	1.91	1.99	1.95	1.92
	Quick Ratio	1.66	1.34	1.38	1.29	1.24
BHP Group PLC	Current Ratio	1.14	1.85	2.51	1.89	1.62
	Quick Ratio	1.16	1.53	2.24	1.58	1.33
Mechel PAO	Current Ratio	0.11	0.13	0.14	0.15	0.16
	Quick Ratio	0.05	0.06	0.06	0.06	0.06
Rio Tinto PLC	Current Ratio	1.52	1.61	1.66	1.91	1.56
	Quick Ratio	1.20	1.29	1.35	1.58	1.24
Vale SA Brazilian	Current Ratio	1.47	2.01	1.45	1.67	1.23
	Quick Ratio	1.13	1.71	1.15	1.18	0.92

Tab. 1.Wskaźniki bieżącej i przyspieszonej płynności finansowej w spółkach wydobywczych o zdywersyfikowanej działalności w latach 2015 -2019. Źródło: opracowanie własne na podstawie Ratios – Key Metrics zaczerpniętych z bazy Reuters

- macroeconomic economic situation, fiscal and monetary policy, degree of financial market development, currency policy, labour costs, purchase prices of production factors. Macroeconomic factors depend on the phenomena and processes occurring across the entire economy.
- sectoral the specificity of the industry, level of industry development and modernity, level of industry risk, prospects of industry development.

Another criterion yet in the classification of factors affecting liquidity is the type of such factors. In this classification, factors are divided into those that are dependent on and those that are independent of the company (Wędzki 2003, p. 73). Factors dependent on the company involve the production technology used by the company, type of industry, management method and financial strategy. They all affect all components of net working capital. However, some components of this type of capital are affected by such determinants as cash flow volatility, the rate of profitability of sales, and the current expected rate of return on operating assets. Factors independent of the company affect all or certain components of the working capital and include the current and expected economic situation, the tax rates and other levies charged to the company, the level of interest rates affecting the cost of capital, the availability of capital from banks and the capital market, the degree of information asymmetry, the sector-specific rate of return on investment. In companies, there exists a strong correlation between factors dependent on the company and those that are independent of it, hence it is practically impossible to determine the impact of a specific factor on the company's liquidity. The company's management board must be knowledgeable about the determinants of financial liquidity, observe the company's economic, legal and social environment and react in a timely manner so as not to lose short-term financial equilibrium.

The liquidity level in mining companies is influenced by both external and internal factors arising from management's decisions. The former includes the economic situation and competition on the coal market, coal prices on exchanges, the rate of transformation from coal to other energy carriers, interest rates and exchange rates. Internal factors, on the other hand, are related to the rate of conversion of individual components of current assets to cash. The greater the share of highly liquid assets in current assets and the longer the payment time for current liabilities, the better the liquidity. The liquidity level in mining companies is undoubtedly influenced by the size of the company, the stage of its life cycle, the specificity of industry processes, the arrangement of logistical chains supporting processes from mining to marketing to further processing.

A good knowledge of liquidity determinants facilitates the management of the company's finances and is important in all economic conditions. It is crucial in times of economic downturns. Economic downturns verify companies' ability to survive in a competitive market. When one company loses liquidity, it sends ripples far and wide, causing payment problems in other entities and contributes to payment gridlocks in the economy. When demand declines during an economic slowdown and this is combined with payment gridlocks, it often means that maintenance of liquidity at all costs becomes the company's management's most important goal, and the adjacent costs are overlooked. Increasing shareholder value becomes a secondary consideration.

Research Methods

Twelve global mining companies listed on several stock exchanges were studied. These concerns can be divided into two groups. The first consists of entities with diversified mining activities and includes the British concern Anglo American, global concern BHP Group, Australia's Rio Tinto, Brazil's company Vale SA and the Russian corporation Mechel. In addition to coal, they also extract other raw materials located in the area for which the concern has obtained a mining license. The British Anglo-American prospects for copper, zinc, nickel, iron ore and diamonds. The BHP Group explores, produces and processes minerals such as coal, copper and iron ore as well as oil and gas. The copper segment is focused on the extraction of copper, silver, lead, zinc, molybdenum, uranium and gold. The coal segment is centred around the extraction of coking and thermal coal. The Anglo-Australian company Rio Tinto focuses on extracting various types of minerals. The Brazilian mining concern Vale S.A. is the largest producer of iron ore and nickel in the world. It also produces manganese, ferroalloys, copper, bauxite, potassium and cobalt. Russia's global coal and metallurgical corporation Mechel produces coal, iron ore, steel, rolled products, ferro-alloys, heat and electricity. Such a diversified range of operations smoothens

Tab. 2. The cash cycle in mining companies pursuing diversified activities, 2015-2019. Source: own calculations based on Ratios – Key Metrics retrieved from a Reuters database

Company	Ratio	2015	2016	2017	2018	2019
Anglo American PLC	Avg. Invent. Days	103.5	92.4	97.6	97.8	101.9
	Avg. A/R Days	40.8	37.7	31.3	27.1	26.0
	Avg. A/R Days	41.8	39.3	46.8	50.4	53.2
	Avg. A/R Days	102.5	90.8	82.1	74.5	74.7
BHP Group PLC	Avg. Invent. Days	128.3	127.5	108.2	103.5	111.0
	Avg. A/R Days	55.7	34.6	26.4	28.0	31.2
	Avg. A/R Days	170.7	196.9	167.8	172.9	174.6
	Avg. A/R Days	13.5	(34.8)	(33.1)	(41.3)	(32.3)
Mechel PAO	Avg. Invent. Days	86.5	88.1	83.6	83.8	77.3
	Avg. A/R Days	32.4	28.1	27.5	25.6	26.2
	Avg. A/P Days	63.7	59.6	46.0	44.6	41.9
	Cash Cycle Days	55.1	56.6	65.1	64.9	61.6
Rio Tinto PLC	Avg. Invent. Days	65.1	60.2	59.7	63.7	64.8
	Avg. A/R Days	31.1	30.3	30.1	28.7	35.4
	Avg. A/P Days	46.2	54.7	57.3	60.1	58.2
	Cash Cycle Days	50.0	35.8	32.5	32.4	32.0
Vale SA Brazilian	Avg. Invent. Days	66.5	48.1	42.5	43.7	44.3
	Avg. A/R Days	39.6	24.7	18.1	17.1	18.6
	Avg. A/P Days	42.5	31.6	30.9	21.9	17.9
	Cash Cycle Days	63.7	41.2	29.7	38.9	45.0

Tab. 2. Cykl konwersji gotówki w spółkach wydobywczych o zdywersyfikowanej działalności w latach 2015 -2019. Źródło: opracowanie własne na podstawie Ratios – Key Metrics zaczerpniętych z bazy Reuters

Avg. Inventory Days - Average Inventory Days Avg. A/R Days - Average Accounts Receivable Days Avg. A/P Days - Average Accounts Payable Days Cash Cycle (Days)

financial results, as short business cycles do not occur simultaneously across all sectors. Losses in one area are compensated for by profits from other activities.

The second group consists of entities is focused on the coal segment. The largest players include the American companies Arch Resources and Peabody, the Indian company Coal India, the Australian company Whitehaven Coal Ltd. and the Russian company Raspadskaya. The activity of Polish companies LWB SA and JSW SA is focused only on coal mining, processing and transport. LWB SA has a logistical link with a power plant. JSW SA, on the other hand, focuses mainly on the extraction of coking coal.

To assess mining companies' liquidity, use was made of static liquidity ratios, and Days Inventory Outstanding, Accounts Receivable Days, Accounts Payable Days and the Cash Cycle. Their values were extracted from a Reuters database. The inventory cycle was determined as the ratio of the inventory balance at year end and the cost of goods sold. The fact that this cycle calculates production costs rather than sales revenues eliminates its large fluctuations caused by changes in coal prices and sales revenues. The Accounts Receivable Days is the ratio of accounts receivable to sales revenues, and the Accounts Payable Days is the ratio of accounts payable to the cost of goods sold. The cash cycle is Accounts Receivable Days plus Days Inventory Outstanding less Accounts Payable Days.

Liquidity Levels in Companies Surveyed

The static liquidity ratios in mining companies with diversified activities are presented in Table 1.

The values of the liquidity ratios are high and, in some years, higher than the normative standards recommended for

these ratios. The values depend on the financial policy around inventories and accounts receivable, terms of payment for deliveries, which is influenced by external factors, including primarily the economic situation and the prices of raw materials. Mechel's ratios are far removed from the rational level. The company reports a high level of unsettled losses from previous periods and has negative equity. Its current liabilities are used to finance operating activities and non-current assets.

A more accurate picture of liquidity than that afforded by static liquidity ratios is painted by the cash cycle, which determines how quickly the company realises cash from inventories and accounts receivable and at what time it settles its maturing accounts payable. The cash cycles of mining companies with diversified operations presented in Table 2 show that they keep large inventories of extracted raw materials. In 2019, in Anglo-American which extracts raw materials on all continents, the Days Inventory Outstanding exceeded 100 days. BHP Group, the world's largest mining concern, kept inventories for almost 4 months. These inventories facilitate the timely delivery of raw materials to many countries. In the three remaining companies, the level of inventories oscillated around 60-80 days. At Vale SA, the figure fell from 66 to 44 days.

The size of inventories does not depend merely on the type of extracted raw materials, but also on the type of transport used, distance to recipients, logistics systems and links with power plants. For example, the Brazilian mining concern Vale SA owns nine power plants and a large network of railways, ships and ports, which facilitates the transport of manufactured products. In the Russian coal and metallurgical corporation Mechel, all of the Group's companies operate within Tab. 3. Current ratio in companies focused on coal mining activities, 2015-2019. Source: own calculations based on Ratios – Key Metrics retrieved from a Reuters database

Company	Ratio	2015	2016	2017	2018	2019
Arch Resources Inc.	Current Ratio	0.21	2.81	2.49	2.67	2.27
	Quick Ratio	0.17	2.45	2.10	2.29	1.85
Coal India Ltd.	Current Ratio	2.31	1.59	1.37	1.51	1.72
	Quick Ratio	2.04	1.37	1.23	1.39	1.59
JSW SA	Current Ratio	0.37	1.02	1.37	0.95	0.96
	Quick Ratio	0.25	0.88	1.57	0.77	0.64
LWB SA	Current Ratio	1.59	1.16	0.98	1.07	1.98
	Quick Ratio	1.33	1.07	0.90	1.05	1.71
Peabody Energy Corp.	Current Ratio	0.18	2.07	1.76	1.85	1.65
	Quick Ratio	0.14	1.86	1.53	1.58	1.31
Raspadskaya PAO	Current Ratio	1.12	0.69	0.99	1.60	3.37
	Quick Ratio	1.03	0.65	0.65	1.48	3.11
Whitehaven Coal Ltd.	Current Ratio	1.22	1.30	1.40	0.94	1.25
	Quick Ratio	0.84	0.91	0.94	0.59	0.81

Tab. 3. Wskaźniki bieżącej płynności finansowej w spółkach skoncentrowanych na wydobyciu węgla w latach 2015-2019. Źródło: opracowanie własne na podstawie sprawozdań spółek węglowych oraz Ratios – Key Metrics zaczerpniętych z bazy Reuters

Tab. 3. Current ratio in companies focused on coal mining activities, 2015-2019. Source: own calculations based on Ratios – Key Metrics retrieved from a Reuters database

Tab. 3. Wskaźniki bieżącej płynności finansowej w spółkach skoncentrowanych na wydobyciu węgla w latach 2015-2019. Źródło: opracowanie własne na podstawie sprawozdań spółek węglowych oraz Ratios – Key Metrics zaczerpniętych z bazy Reuters

Company	Ratio	2015	2016	2017
Arch Resources Inc.	Avg. Invent. Days	32.1	32.8	24.1
	Avg. A/R Days	26.2	31.5	32.(
	Avg. A/P Days	25.6	23.7	22.9
	Cash Cycle Days	32.7	40.6	33.2
Coal India Ltd.	Avg. Invent. Days	48.7	52.9	44.5
	Avg. A/R Days	87.7	104.0	113.3
	Avg. A/P Days	20.4	21.5	30.5
	Cash Cycle Days	115.0	135.4	127.4
JSW SA	Avg. Invent. Days	27.0	27.8	27.3
	Avg. A/R Days	41.1	40.9	35.8
	Avg. A/P Days	113.7	135.4	131.4
	Cash Cycle Days	(45.6)	(66.8)	(68.3)
LWB SA	Avg. Invent. Days	20.8	22.4	28.6
	Avg. A/R Days	55.7	53.9	50.0
	Avg. A/P Days	63.9	74.9	134.5
	Cash Cycle Days	12.7	1.3	(56.0)
Peabody Ener. Corp.	Avg. Invent. Days	27.9	22.8	22.5
	Avg. A/R Days	25.8	27.2	33.6
	Avg. A/P Days	31.0	27.7	30.7
	Cash Cycle Days	22.7	22.3	25.4
Raspadskaya PAO	Avg. Invent. Days	38.4	35.1	36.7
	Avg. A/R Days	111.5	285.4	225.(
	Avg. A/P Days	28.2	46.4	46.5
	Cash Cycle Days	121.8	274.2	205.1
Whitebayen Coal Ltd	Avg Invent Davs	66.5	48.1	42 5

| Whitehaven Coal Ltd. | Avg. Invent. Days

a single production chain – from raw materials to high added value products. The BHP Group has a negative cash cycle resulting from much longer payment terms for amounts payable than amounts receivable.

Table 3 shows the liquidity ratios of companies extracting primarily coal. The diversification of their activities is the result of either coal processing processes, coal's use in heating or auxiliary processes connected with the mining processes.

All the companies surveyed reported high liquidity ratios and these fall within the normative range. In 2019, many companies saw their liquidity ratios rise. JSW SA'S ratios were the lowest among the companies surveyed. It does not mean, however, that the company does not settle its liabilities on time. The level of ratios depends on the one hand on the method of recognition of current assets, and on the other hand, on the financial policy regarding inventories and accounts receivable. Inventories are shown in the balance sheet at the cost of production. The cash realised from their sale is much higher than this cost because the price of coal in normal economic conditions includes, in addition to production costs, also cost of goods sold, general and administrative expenses and profit. In line with the principle of conservatism, in the balance sheet, accounts receivable are recognised at their net value, i.e. after adjusting entries related to the risk of their non-realisation of cash. Additionally, current assets do not reflect the fact that the company constantly generates funds through day-to-day operations, and these can be used to pay off maturing current liabilities. The fact that companies can settle their liabilities out of available factoring and credit lines is also disregarded. These are not reported in the balance sheet until the company has used them. They can constitute a potential liquidity cushion, as can the difference between the book and market value of inventories and accounts receivable.

The specificity of mining processes necessitates the use of the cash cycle consisting of partial Days Inventory Outstanding, Accounts Receivable Days and Accounts Payable Days to assess financial liquidity. Mining companies keep inventories of raw materials to ensure that they can continue to supply customers. Polish companies maintain smaller coal inventories than their global counterparts. JSW's inventories on average cover 30 days, as do to Peabody's, which supplies coal to the US domestic market. LWB SA has only 20 days of coal in stock. Coal exporting companies' inventories must be even larger. (Table 4).

Coal companies have lower levels of inventories of raw materials than companies with diversified mining activities. Characteristically, Polish coal companies report a negative cash cycle resulting from a longer deferral of settlement of accounts payable, which exceeds the time needed to realise accounts receivable. India Coal and Raspadskaya report exceptionally long cash cycles. In Raspadskaya in 2016, the cycle was 274 days on account of very long Accounts Receivable Days. In 2016, the company waited 285 days for settlement of debts by buyers. Coal India has a similarly long waiting period. On the other hand, very long waiting periods for settlement of accounts payable occur in BHP Group companies and JSW SA. In other coal companies, they average 30-60 days.

Conclusions

Liquidity maintenance underpins efficient company management. Rational liquidity management decisions depend on whether managements have or do not have reliable information at their disposal. In the mining industry, the commonly used liquidity ratios are not enough to guarantee rational decisions about liquidity and can only serve to provide certain information. The specificity of mining manifests itself, inter alia, in high levels of inventories of extracted raw materials. An increase in inventories causes the current ratio to increase, and its level above the accepted normative values is often construed as excess liquidity. Meanwhile, an increase in liquidity ratios resulting from an increase in inventories indicates deteriorating liquidity. Mining companies, especially those which pursue diverse activities extracting various resources, have a high current ratio. These companies maintain a higher level of inventories than those entities which are focused only on coal mining. Moreover, inventory levels depend on the distance to markets and the need to ensure continuity of supplies. Lower inventories in coal companies are often due to logistical links with coal-consuming power plants. The resulting lower liquidity ratios are not indicative of lower liquidity.

Static measurement of liquidity is insufficient to properly monitor companies' ability to settle their debt in a timely manner. Such measurement is supplemented with data on the cash cycle and its constituents – Days Inventory Outstanding, Accounts Receivable Days and Accounts Payable Days. Accounts Receivable Days and Accounts Payable Days illustrate the company's trade credit policy, which plays a key role in liquidity maintenance.

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Problemy pomiaru płynności finansowej spółek górniczych

Umiejętność sterowania płynnością finansową ma znaczenie w każdych warunkach gospodarczych. Szczególnie ważna staje się w warunkach dekoniunktury. Jest ona uwarunkowana posiadaniem wiarygodnych informacji o poziomie płynności finansowej. Takich informacji nie zapewniają statyczne wskaźniki płynności finansowej. Ich wysoki poziom wynika z utrzymywanych wysokich stanów zapasów wydobywanych surowców i nie wskazuje na nadpłynność finansową. Dodatkowych informacji dostarczają cykle konwersji gotówki i składające się na nie cykle zapasów, należności i zobowiązań krótkoterminowych. Długie cykle konwersji gotówki wskazują na krótszy czas odroczenia płatności zobowiązań wobec dostawców i niższy poziom płynności finansowej. Dla zachowania płynności finansowej spółki muszą utrzymywać na kontach wyższe stany środków pieniężnych. Cykle krótkie mogą natomiast wynikać z przeterminowania płatności faktur co znajduje odzwierciedlenie w długich cyklach zobowiązań krótkoterminowych. Niektóre spółki węglowe mają bardzo długie cykle zobowiązań i ujemne cykle konwersji gotówki. Oznacza to że część aktywów trwałych finansują zobowiązaniami krótkoterminowymi.

Słowa kluczowe: płynność, wskaźniki płynności, cykl gotówkowy


The Aspects of Sustainable Development in Mineral Resources Management

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Abstract

Mineral resources provide a high standard of living for modern societies: satisfying electricity demand as well as demand for construction materials and they sustain the basis for industry and technological development. Now, modern societies are facing the challenge of reversing the trend of the depletion of non-renewable mineral resources and sustainable development is intended to ensure the survival of human civilization in the face of dwindling non-renewable raw materials (especially energy resources) and also increasing anthropopression and related environmental pollution. The amount of non-renewable mineral resources of the Earth's crust is limited. Under specific conditions there is a possibility of their regeneration however over a period of several if not more than a dozen generations. The article raises questions how societies can prevent mineral resources crises in future and whether this task is feasible. The article identifies the main aspects of the sustainable development in mining sector in Poland as well as environmental challenges related to the new CSR mechanism which are: the creation and implementation of sustainable and responsible business model which thanks to reformed financial and economic system, will make creating a better future easier, more natural and more cost-effective. The crucial aspects of sustainable development as economic and social conditions, environmental challenges, safety of agglomeration located in the area of exploitation of resources or in its neighborhood were also presented in the article. The author highlighted the legal conditions for the management of deposits and extracted mineral resources as well as work safety and research and development activities in the sector.

Keywords: mineral resources, sustainable development, research and development expenses

Introduction

Today, the concept of sustainable development is widely used in many areas of human life. It appeared for the first time in the second half of 20th century as a reaction to negative environmental consequences of dynamic economic growth which often occurs with uncontrolled and too intensive use of natural resources. Under the auspices of the United Nations, at the end of the 1960s they were taken the actions to prevent a world-unfavorable phenomenon which were included in the World Commission on Environment and Development Report from 1987: Our Common Future. In Poland, the principle of sustainable development is enshrined in the constitution. Its definition is contained in The Act of 20 May 2020 Environmental Protection Law (Journal of Laws - Dz. U. 2020, item 1219, consolidation).

The aim of the paper is to prove that the principles of sustainable development in extractive industry are not respected at all or only partially. The basic research questions are following:

- 1. Whether companies apply the principle of sustainable development in a comprehensive manner?
- 2. Whether there are conditions for the application of the principles of sustainable development. Moreover, there is a need to ask a question?
- 3. If the entities analyze and report the results of these activities, recognizing information as the main feature of prosocial behaviors in sustainable development?.

The responses that need to be found to these questions allow the verification of the main hypothesis which assumes that not all companies apply the principles of sustainable development which are derived from its definition. The part of companies applies the principles, but not to the full extent.

In order to deepen the verification, the author formulates the sub-hypotheses:

- 1. There is significant untapped potential for companies' building awareness in a sustainable development sphere.
- 2. Law and legislation conditions are insufficient to build companies' sustainable development awareness.

In the article were used qualitative comparative methods [Nadolna, 2009, p.140] and Individual In-depth Interview method (IDI) which were conducted as part of the statutory research conducted in 2019 and 2020 by The Collegium of Business Administration Warsaw School of Economics in Warsaw in which the author participated as a member of the research team. Within the quantitative methods the author employs statistical methods. Furthermore, the critical content analysis with existing data analysis was also conducted.

A sustainable organization is based on Triple Bottom Line (TBL) theory which combines social, environmental and economic goals. These objectives are realized through collaboration between the organization and customers, suppliers, local communities and other stakeholders. The short-term statutory aims as well as additional ones including: the will to learn, Tab. 1. Documented balance and industrial mineral resources in Poland as od 31.12.2019 in million tones or m³. Source: own elaboration based on:: The balance of mineral resources deposits in Poland as of 31.12.2019 Polish Geological Institute-National Research Institute (PGI-NRI) 2020, Warsaw, www.teraz-srodowisko.pl/media/pdf/aktualnosci/8930-bilans-zloza-kopali-2019.pdf [access: 23.01.2021]

Type of mineral	Amount deposit	of		Total amount of	Including:		
deposit	total	active	Extraction	deposit in m t/ m/ m³	Balance deposit	Off balance deposit	Industrial deposit
Natural gas	305	201	5.0	219 202.5	141 971.4	2 277.7	74 953.4
Petroleum	87	57	0.94	36.0	22.6	0.40	13.0
Lignite	91	9	52.9	27 773.8	23 261.8	3 517.5	994.5
Hard coal	162	46	64.1	82 462 8	64 329.8	13 353.8	4 779.2
Zinc and lead ores	21	3	1.5	151.9	92.2	55.9	3.8
Copper ore	13	6	29.88	3 909.8	1 951.2	8 01.3	1 157.3
Rock salt	19	6	4.7	22 017 72	90.32	20 160.5	1 766.9
Gypsum and anhydrite	15	4	1.1	340.2	253.9	20.0	66.3
Crushed stones and block stones	742	316	78.7	15 645.7	11 543.3	529.1	3 573.3
Limestones and marls for cement industry	69	20	28.2	15 668.7	12 694.8	953.3	2 020.6
Sand and gravel	10 504	3 886	182.8	24 321 3	19 742 7	409.8	4 168.8
Peats in total	298	81	1 189.0	134.59	92.42	6.54	35.63

Tab. 1. Udokumentowane zasoby geologiczne bilansowe, przemysłowe stan na 31.12 .2019 rok w mln ton lub m³

rationality, alignment, motivation and empowerment [Lozano R, 2008, pp. 499-509] shall be included in a long-term strategy which allow to achieve the aforementioned objective.

A cost-benefit analysis should not be drawn up for each of these elements separately but for all of them together in accordance with the principle of sustainable development.

Thus, the implementation of sustainable development is a process of continuous integration of activities in such key areas as:

- technical-economic area ensuring economic growth
- ecological area guaranteeing the raw materials and environment protection
- social area ensuring that the common social and environmental objective is achieved within the framework of Corporate Social Responsibility and Corporate Sustainability and Responsibility.

The statutory research conducted in 2019 and 2020 in Warsaw by The Collegium of Business Administration Warsaw School of Economics shows that 37.5% of survey respondents are aware of the base definition, of which the largest (80%) percentage concerned production companies. In the service industries, the conscious balance of economic, social and ecological objectives indicates 14.3% of respondents. There was a negative answer in the administration section. It was found that:

- 50% of respondents understand the base definition in one or at most two aspects i.e. ecological or combination: ecological-economic aspect or ecological-social aspect etc.
- Seven (7) respondents which is 43.8% of surveyed people have taken specific actions in the field of sustainable development.
- One (1) company indicates sense of security as an important aspect of sustainable development
- Only 12.5% of the surveyed companies indicate the link between activities undertaken in the area of sustainable development and the size of the organiza-

tion, the industry in which its operates, as well as the organizational culture of the company and the region of organization origin.

Based on comparative thinking with analyzing these results it can be assumed that companies from mining sector present a similar understanding of the principles of sustainable development. When analyzing an understanding of the notion sustainable development, it should be noted that in case of activities relating to the exploitation of mineral resources, this term acquires a very specific meaning. It is inherent in this activity that include non-renewable resources therefore the first and crucial principal of sustainable development must be rational and economical both the extraction and use of mineral resources (Dubiński, 2013, p.2).

1. The rational exploitation and use of natural resources. Preserving natural resources.

Mineral resources are the materials of intrinsic economic interest extracted from deposits. Mineral resources occurring in Poland are classified into following basic groups, i.e.

- Energy resources: hard coal, lignite, natural gas, peat;
- Chemical raw materials: rock salt, gypsum, sulphur;
- Metal ores: zinc and lead deposits, molybdenum-tungsten-copper ores, iron ore
- Natural stones: sandstone, limestone, marls, dolomites, sand, gravel, clays
- Healing water

Mineral resources extracted and used by humans have always been a condition for the economic growth and civilization development of societies and states which was clearly reflected during The World Mining Congress: Everything begins with mining which took place in USA in 2000. (...) Many areas, both in the past and in the modern times, used the development of mining to their own development [Dubiński , 2013, p.2]. In the publication The balance of mineral resources deposits in Poland prepared by Polish Geological Tab. 2. The economy of the Silesian Voivodeship in the context of mining activities in the period 2010-2018. Source: own elaboration based on Central Statistical Office (CSO) Silesian Voivodship (2018), www.katowice.stat.gov.pl/opracowania-biezace/opracowania-sygnalne [access 30.01.2021]

Tab. 2. G	Gospodarka	województwa	śląskiego w	kontekście	działalności	wydobywczej	w latach 2010-2018

Years	2010		2015		2017		2018	Dynamics in % 2018: 2010
		The sole	d indust	ry output (ir	n million	s of PLN)		
Total								
including:	173623.3	193638.7	111.5	221 533.3	114.4	233 039.2	105.2	134.2
public								
sector	37833.0	27 978.2	74.0	31 404.1	112.2	33 282.9	106.0	88.0
private								
sector	135790.3	165660.5	122.0	190 128.2	114.8	199 756.3	105.1	147.1
			The r	nining indust	try			
Total,								
including:	23 162.7	21 351.9	92.2	23 368.5	109.4	24 678.6	105.6	106.5
coal and lignite	22 462.1	19 514.1	88.1	21 393.0	109.6	22 332.9	104.4	99,.4
other mineral resources	700.6	1 837.8	262,3	1 975.5	107.5	2 345.7	118.7	334.8
The perce	entage share	e of sold pro	duction Sil	of mineral re esian region	esources	in the total	sold pro	luction in
	13.34	11.02	х	10.54	х	10.58	х	х

Institute-National Research Institute (PGI-NRI) presented data on 14 247 domestic mineral raw materials deposits documented in Poland as of 31.12.2019.

Table 1 provides the total mineral resources split for balance, off-balance and industrial, as well as total amount of deposit including active ones and finally average annual extraction of minerals.

Some discrepancies between the number of documented deposits (12 326) and the number of active deposits with exploitation (4 635) is only 37,6% and is caused by the fact that existing legislation about including mineral deposits in the local spatial development plan do not guarantee the security of access to deposits for exploitation purposes. Another substantial barrier in starting the exploitation is the ownership of mineral deposits (mostly in private lands) located in the near-surface zone with the ownership of the land property. The further limitation is that decisions on the arrangement of the area are made by municipalities and they are often based on particular interests of local lobby [Radwanek-Bąk, 2010, p.4].

2. The key elements of sustainable development

The public acceptance of modern mining which has negative impact on environment and causes less or more discomfort to people who live in mining areas and their neighborhood is crucial for its activity. The need for sustainable management of mineral resources applies to all stages of deposit management: to begin with documentation, through exploitation, material excavation, use of final raw material and then secondary raw material. In the light of presented mineral deposit base and the prospects for Polish mining industry it can be concluded that the only reasonable approach is to maintain sustainable mining and sustainable management of mineral resources. Despite the mentioned statistics about companies exploited mineral resources in Poland, the wellknown from its mining tradition is

Despite the statistics mentioned, the mining companies are operating mineral resources, Silesia is the most famous for its mining traditions. Silesia region covers an area of 12 290.4 square kilometers, which represents 3.9% of the country. It is inhabited by 4 616 million people which is 12% of the country's population. This region is also characterized by the highest population density in the country which is 375 people/km2. GDP per capita is PLN 39.7 thousand/ 1 inhabitant which represents 107% of the average national GDP. For these reasons, the Silesian Voivodeship is used in the article to illustrate the technical and economic conditions determining economic growth as a basis of sustainable development.

Economic growth for the business entities in mining sector means the long-term stability both in the planned production output as well as satisfying the requirements of customers and finally achieve the economic efficiency by selling the extracted resources. The data presented in Table 2 specifies the sold production of mining industry in the Silesian region: over the last decade there has been a systematic decreasing in the share of the sold production of mining industry in the general industry sales (from 13.34% in 2010 to 10.58% in 2018.)

3. The environmental challenges – the operational security of agglomerations on the area of exploitations or its neighborhood

The environmental challenges are the major problems for the mining of all types of deposits. The requirements relating to the protection of living environment and landscape are the potential sources of conflict. These challenges comply with the second pillar of sustainable development. In global mining, these challenges cover a wide range of problems and covers all elements of the environment, meaning the surface of the earth, water and air.

Practically every mining activity affects the natural environment to some extent [Dubiński, 2013, p. 4]. Above all, this activity causes the changes: ground deformations – depressions; horizontal deformations, discontinuous deformations etc., seismicity induced by mining activities, changes of water relationships, soil sterilization, dusts and gases emissions, noise and others. Under European Union law and Polish law Tab. 3. The total number of economic entities running mining activities of mineral resources in Poland. Source: own elaboration based on: National portal of mineral and raw materials http://surowce-kopalnie.pl/ [access: 11.02.2021] and GPW Main Market https://www.gpw.pl/spolki [access: 11.02.2021]

Tab. 3. Liczba podmiotów gospodarczych ogółem prowadzących działalność wydobywczą surowców mineralnych w Polsce

Total producers	number	%
GPW Non-listed Companies	321	96.7
GPW Listed Companies	11	3.3
Total	332	100.0

there is a great emphasis on the necessity to conduct public consultations. This issue is regulated in the Constitution of the Republic of Poland as well as in the above-mentioned legal regulations.

Social problems related to the extraction of mineral resources often take the form of social conflicts which have twofold sources:

- Companies do not take into account social and environmental aspects in their activities choosing the economic aspects as priority. Sometimes the value of social and environmental elements are incorrectly determined as a part of the balance of profits and losses for individual geological and mining projects.

- Society rejects projects where, although social and environmental elements have been taken into account and correctly valued but it has been found that the net economic benefits are higher than the net losses to the society and the environment. The lack of social acceptance in this case may be due to the following reasons:

- The lack of information meaning no detailed information about planned and ongoing projects in the context of sustainable development.
- Lack of public awareness and education in the field of sustainable development. Furthermore, in extreme cases, providing the society with incorrect information, for example, creating an image of mining as industry based on outdated, environmentally aggressive technology in the media and schools. Lobbying ecological groups and economic potentates who often declare that they care for the environment and the public good but they really protect their own interests;
- NIMBY phenomenon (not in my backyard) refers to the propensity of local citizens to insist on siting unwanted but important and necessary facilities anywhere but nowhere near them.

The major problem remains the conflict of interests between companies and local authorities which striving to win as many voters as possible, often act opportunistically and shortsightedly.

To ease currency tensions and conflict situations the following actions should take place:

- Initiating information campaign on sustainable development for local communities and municipal authorities; promoting knowledge about sustainable development as well as finding methods of popularizing knowledge about the importance of raw materials for the development of the economy, including introducing the issue of raw materials to the curricula of schools and universities. - A legal warranty that the municipality will allocate part of the mining fee to the investment e.g. the construction of infrastructure and job creation which might compensate local communities for negative impact of mining activity to environment.

- Promoting Corporate Social Responsibility in strategies of companies – not only economic ones but also social and environmental aspects. Bearing in mind that application of Corporate Social Responsibility is optional, the benefits of its use should be communicate to the companies e.g. a positive image for the company and therefore increasing its value.

- Promoting the benefits of dialogue with local communities using reliable information

Promoting good practices concerning the sustainable development. The European Commission has recognized as good practice the process of opening the mine Wolfram Bergbau und Hütten AG in Austria. The mine is located in a nature reserve near the national park and its construction required the reconciliation of tourist and natural assets with the extraction of raw materials. The cooperation between pro-ecological groups, local community, investors, the nextdoor neighbors and other stakeholders was the key to the success. The another example of good practice is initiative Towards Sustainable Mining (TSM) prepared by the Mining Association of Canada (MAC) and recently also adopted in Finland. The main three TSM guiding principles are: engaging and supporting dialogue with community, protecting the health and safety of the employees, contractors and communities and practicing continuous improvement in all facets of mining operations.

Another example is the activities of Swedish LKAB company which declared to purchase all properties in old Kiruna city and relocated it three kilometers to the East. Kiruna is located on valuable iron ore which exploitation is threatening the city that is why LKAB has taken steps to take into account the needs of residents and reindeer breeders. The whole process of moving the city will take at least 20 or 30 years. It will cost approximately one billion dollars [Nowacka- Isaksson, 2015].

The Silesian – Opole region is associated with mining in Poles awareness. The history of local exploitation and mining traditions of this region cast many centuries back. During the Neolithic Age the flint was mined with earthworks in the neighborhood of Raciborz. During the first centuries A.D. the iron ore was exploited in the same region [Molenda, 2005, pp.187-196]. Currently in Poland there are 332 economic entities operating in the mineral resources sector and 3.3% (11) of them are listed on the capital market of the Warsaw Stock Exchange. Tab. 4 . Employment and workplace accidents in the Silesia region in 2010-2018. Source: own elaboration based on CSO Silesian Voivodship (2018) www.katowice.stat.gov.pl/opracowania-biezace/opracowania-sygnalne [access 30.01.2021]

Years	2010	2015		2017		2018		Dynamics in % 2018: 2010
The average employn	nent in the ir	ndustry (the n	umber o	f employees	5)			
Total including:	440 604	425 324	96.5	435 208	102.3	442 013	101.6	100.3
in coal and other raw materials mining	119 006	98 402	82.7	84 662	86.0	85 316	100.8	77.6
% share of people employed in the mining industry in total employment in industry								
	27.0	23,1	х	19.4	х	19.3	х	x
		Working co	onditions	– safety – ir	njured			
Total, including:	13 802	12 156	88.1	12 265	100.9	12 026	98.1	87.1
In industry overall including:	х	×	х	х	x	5 903 (49.8%)	x	x
Mining and extraction	x	x	х	x	x	1 524 (25.8%)	x	x
% share of people inj	ured in accio	lents at work	in emplo	byment in in	dividual	years		
In industry overall	3.13	2.85	х	2.81	х	2,72	х	х
In mining	11.59	12.35	х	14.48	х	14.09	x	x

Tab. 4. Sytuacja zatrudnieniowa i wypadkowa w regionie śląskim w latach 2010-2018

On the basis of detailed author's own research carried out on the basis of existing data concerning the entities listed in Table 2 it can be noticed that only 11.7% (39) entities from mineral resources sector fully apply the sustainable development principles and they are all listed companies and 28 from unlisted companies. These entities disclose information about implemented sustainable development principles which can be found in the updated reports and information to customers.

In the group of non-listed entities only 50 partially apply the principles of sustainable development which are limited to the use of the integrated management system. This should be strongly underlined because the responsible and effective management, as well as ISO14001 that specifies requirements for an effective environmental management system in organizations, are crucial for sustainable development, economic progress and increased security of raw materials, both nationally and throughout Europe. These entities account for 15.1% (150) of the entire surveyed population.

With regard to the remaining 243 companies only economic performance was found. No pro-ecological and pro-social performance were found indicating any sustainable development awareness which is equivalent to lack of information on this subject.

4. Legal conditions for the management of deposits and mineral resources

National Development Strategy 2020 which emphasizes the main goals for country development in medium term as well as Innovation and Efficiency of the Economy Strategy (SIEG) and Strategy for Energy Security and Environment which are two from nine integrated strategies which serve to implement objectives included in medium term strategy. These documents are the only ones that provide the subject of deposits and so far they have determined a differentiated approach to the management of non-energy raw materials and Energy raw materials in Poland. The same distinction between Energy and non-energy raw materials was made in European Union policy. Until the finalization of The Energy Policy of Poland up to 2050 the Action Plan for the non-energy raw materials supply security shall be applied.

In Poland the institutional competences in the area of non-energy and non-renewable resources are not centralized. The specific aspects of the policy in this area can be assigned to the following organs of state administration (according to The Act of 4th September 1997 on Branches of Government administration, amended 19th November 2015), management of mineral deposits (the Ministry of State Assets), economy (the Ministry of Economic Development, Labour and Technology), regional development (the Ministry of Economic Development, Labour and Technology), foreign affairs (the Ministry of Foreign Affairs), construction, planning, area management and housing (the Ministry of Infrastructure), science and higher education (the Ministry of Science and Higher Education), public finance (the Ministry of Finance), treasury (Ministry of the Treasury - since od 15th November 2019 as the Ministry of State Assets), labour (the Ministry of Economic Development, Labour and Technology). Moreover, the geological administration authorities are playing an important role (Chief National Geologist, Marshals of the Voivodships, District Governors), the State Geological Service, the mining supervisory authorities, the Patent Office, the Maritime Offices and institutions controlled by the Prime Minister e.g. CSO, PPO and others.

The legal instruments of the policy in the field of non-energy non-renewable resources in Poland are provided in several legal acts, including, in particular:

Act of 9 June 2011 Geological and Mining Law (Journal of Laws – Dz. U. 2016, item 1131) Tab. 5. Number of entities conducting research activity and the expenditures on research and development activity in the mining industry in 2010-2018. Source: own elaboration based on CSO Silesian Voivodship www.katowice.stat.gov.pl/opracowania-biezace/opracowania-sygnalne [access 30.01.2021] and CSO Research and development activities in 2018 https://stst.gov.pl/obszary-tematyczne/nauka-i-technika-spoleczenstwo-informacyjne/nauka-i-technika/dzialalnosc-badawcza-i-rozwojowa-w-polsce [access 30.01.2021]

Tab. 5. Liczba podmiotów prowadzących działalność badawczą oraz nakłady na działalność badawczą i rozwojową ponoszone w przemyśle wydobywczym w latach 2010-2018

Years	2010	2015		2017		2018	5	Dynamics in % 2018: 2010
Entities conducting R	&D activity i	in the country	/					
Country in total	3 474		4 427		5 102		5 779	x
Entities conducting re	esearch activ	ity (number)	in the S	ilesia region				
Silesia in total	234	493	210.7	627	127.2	622	99.2	265.8
% share to the country	6.7%	x	x	x	x	10.8%	x	×
Expenditure on resea	arch and dev	elopment in I	PLN thou	sand				
Country in total	16 68 000	18061000	111.7	20578000	113.9	25648000	124.6	158.6
Silesia in total	848 800	1 352 200	159.3	1 530 500	113.2	1871 200	122.3	220.45
% share to the country	5.2%	7.5%	x	7.4	x	7.3%	×	×
Expendatiture on innovation activity in PLN thousand								
Total	3 871	3359 642	86.8	3 027 921	90.1	3 118 850	109.6	85.7
including:	815	5555 012	0010	5 62, 521	5011	5 110 050	10510	
Mining and extraction	x	x	x	x	x	213 221 (6.8%)	x	x

- Act of 27 April 2001 Environmental Law (Journal of Laws – Dz. U. 2016, item 672)
- Act of 10 April 1997 The Energy Law (Journal of Laws Dz. U. 2020, item 833, consolidation)
- Act of 27 March 2003 The Law on Land Development (Journal of Laws – Dz. U.2016, item 778
- Act of 2 July 2004 on Freedom of Economic Activity, (Journal of Laws – Dz. U.2016, item 1829)
- Act of 20 February 2015 The Renewable Energy Sources Act (Journal of Laws – Dz. U.2021, item 234, consolidation)
- Act of 3 October 2008 on the Disclosure of Information about the Environment and its Protection, Public Participation in Environmental Protection and Environmental Impact Assessments (Journal of Laws – Dz. U.2016, item 353)
- The Civil Code

A major challenge for the development of coherent raw material policy is the great number of institutions and legal acts as well. And that is not only a problem of Poland, generally, it can be observed in economies all over the world. Since 2015 in Poland have been carried out the works on a document National Raw Materials Policy which contribute to the establishment of the Committee for Sustainable Mineral Resources Management of the Polish Academy of Sciences in April 2018. Till then Poland did not have raw material policy, any vital tools to its performance, legitimate geological service with specific tasks and acting exclusively on behalf of the state and in the interests of the state and society [Hausner (edit.), 2015, p.118]. The preparation of legal acts and documents is an essential core of eco-development in Poland at the government level. These acts shall set the broad lines of activities for sustainable development. According to Smakowski T., Szamałka K, [2016, p. 276] any new legal solutions must take into account mostly EU arrangements in the area of the economy of raw materials which include sustainable development and environmental conditions.

5. Work safety

The mining industry in 21st century, even maintaining the direction of sustainable development, has to guarantee its employees safe working conditions. The issue of work safety due to its complexity is the major challenge for mining science and practice. The constantly increasing depth of exploitation, which is now a global trend, makes work safety a crucial aspect of sustainable development of mining industry.

The technologies used in the exploitation of deposits and the acquisition of mineral resources have to minimize or eliminate the negative effects of mining and extraction processes. Furthermore, a key issue is the development of new technologies of recultivation the exploited areas. The diverse technologies of recultivation of post-mining areas are developed and implemented both in global and Polish mining, and they bring beneficial effects. It should be also stressed that special care for the environment is one of the most important aspects in social responsibility and the achievement of a common social and environmental objective, Since the public awareness that mineral deposits are a non-renewable good is unfortunately poor, its improvement or change of the situation in this area is another challenge that should be followed by specific actions [Dubiński, 2013, p. 5].

The scale of the issue, e.g. the size of employment in industry in the last decade in Silesia region, as well as the number of people injured in accidents related to work in mining industry is presented in table no.4. Both the total employment in 2010-2018 and the number of employees in the mining industry remained unchanged. But the share of employees in the mining industry in total employment in industry decreased significantly from 27% in 2010 to 19.3% in 2018 which is undoubtedly the result of organizational and technological changes in the processes of extracting raw materials and sustainable development regime linked to this sector. What is particularly worrying is that the share of people injured in accidents at work in the mining industry has increased from 11.59 % in 2010 to 14.09 % in 2018 with a reduced accident rate in the total industry.

This situation create a lot of space to institutions which are conducting research and development activities not only in order to gain new knowledge but above all to obtains specific and useful solutions which will minimize the negative effects of human activity in order to protect human life and health. The profitable geological and mining investments as well as research and development prove the success of the properly conducted public policy of raw materials. Table 5 gives an overview on this subject in mining industry. The number of entities conducting research activity in Silesia over the period under study increased more than two and a half times, showing the dynamics of 265.8%, and their share in the total number of entities in R&D in 2018 in the country amounted to 10.8% compared to the share of at the beginning of the decade at 6.7%. Expenditure on research and development activities in Silesia also shows significant dynamics compared to 2010: increased as much as 120.5%, while gross expenditure on R&D in the country increased by 58.6% during this period. Over the decade the share of expenditure on R&D activities in the institutions operating in Silesia in relation to the national ones has increased from 5.2% to 7.3%. Although these figures are insufficient however the upgrade trend that has been observed over the last decade looks promising. Presumably, maintaining the dynamics of positive changes will increase the pace of sustainable development of the mining activity.

Conclusion

The scale of problems related to the management of mineral resources, affecting modern societies, including our country, is disproportionately greater than the scale of activities, programs and projects undertaken in order to solve them. It results from the fact that these activities are limited to the pilot projects which are undertaken only for image enhancement and gaining CSR goals rather than serving to local communities. The research results confirm the main hypothesis of the article that not all companies apply the principles of the sustainable development as it is defined. Some companies apply these rules, but not the full extent of them. The sub-hypotheses presented in the introduction have been confirmed as well. There is untapped potential in Polish mineral resources sector in particular with raising awareness of sustainable development among companies, also the legal conditions are insufficient in this matter.

In addition, the above conclusion is confirmed by the results of the previously cited studies, which show that:

- Companies, to a great extent, confuse CSR principles with sustainable development. Great number of them refer only to the ecological dimension.

- Organizations undertake sustainability actions between financial, environmental and social performance but these actions are coincidental rather than being a part of planned strategy of sustainable development.

- Most of the surveyed organizations are not consciously managed in a sustainable manner (balancing social, economic and social goals) – 63%.

- More than half of the surveyed organizations implement some specific actions for sustainability in the financial, environmental or social area however they do not necessarily connect these 3 aspects – 56%.

The low awareness of entrepreneurs dealing with the mineral resources industry who do not apply the principles of sustainable development, as shown in the research, does not bode well for a quick elimination of socio-economic problems affecting Polish society. In the context of the message from the United Nations Manifesto titled: "Global Economic Ethic -Consequences for Global Businesses" launched on October 6 2009, it is important to shift the pivotal role from the current CSR as Corporate Social Responsibility to CSR as Sustainable and Responsible Business. This change means that the most important factors are "sustainable development" (stemming from the ecological movement), which is the goal that is being pursued through the implementation of challenges, vision and strategy, and "social responsibility". To make the set goals achievable appropriate actions must be taken as well as the proper management of economic and social processes. Therefore, it is a misunderstanding to claim that the purpose of business is to make a profit to its stakeholders. This is only a means to achieve the ultimate goal of acting to benefit society. The final effect of these activities is the provision of safe, high-quality products and services which will contribute in ensuring future generations at least today's living conditions without worsening the existing ecological and social systems. But it will be possible if the sustainable development regime in its three pillars.

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Aspekty zrównoważonego rozwoju w gospodarce surowcami mineralnymi

Surowce mineralne zapewniają wysoki standard życia współczesnych społeczeństw, gwarantując zaspokojenie zapotrzebowania na energię, materiały budowlane, a także stanowią podstawę przemysłu i rozwoju technologicznego. Przed współczesnymi społeczeństwami stoi wyzwanie odwrócenia trendu sczerpywania się nieodnawialnych surowców mineralnych, a zrównoważony rozwój ma zapewnić możliwość przetrwania cywilizacji ludzkiej w obliczu zmniejszających się zasobów surowców nieodnawialnych (zwłaszcza energetycznych) oraz wzrastającej antropopresji i związanego z nią zanieczyszczenia środowiska przyrodniczego. Ilość mineralnych surowców nieodnawialnych w skorupie ziemskiej jest ograniczona, a ich regeneracja możliwa jedynie w specyficznych warunkach w czasie obejmującym kilka jeśli nie kilkanaście pokoleń (Gałuszka, Migaszewski, 2009, s. 123). W artykule stawiane są pytania o to, w jaki sposób społeczeństwa mogą zapobiec kryzysowi surowcowemu w przyszłości i czy to zadanie jest możliwe do wykonania. Mając to zadanie na uwadze należy do koncepcji gospodarki surowcami mineralnymi odnieść się w sposób zgodny z zasadami zrównoważonego rozwoju który ma zapewnić możliwość przetrwania cywilizacji ludzkiej w obliczu zmniejszających się zasobów surowców nieodnawialnych (zwłaszcza energetycznych) oraz wzrastającej antropopresji i związanego z nią zanieczyszczenia środowiska przyrodniczego

W artykule wskazano główne aspekty zrównoważonego rozwoju sektora wydobywczego w Polsce i wyzwania związane z ochroną środowiska naturalnego w kontekście nowego CSR, w którym chodzi o stworzenie i wdrożenie zrównoważonego i odpowiedzialnego modelu biznesowego, który przez zreformowany system finansowy i ekonomiczny sprawi, że tworzenie lepszej przyszłości będzie łatwiejsze, bardziej naturalne i opłacalne. Przedstawiono takie kluczowe elementy zrównoważonego rozwoju jak uwarunkowania gospodarcze i społeczne, wyzwania związane z ochroną środowiska, bezpieczeństwo funkcjonowania aglomeracji na terenach eksploatacji złóż lub w ich sąsiedztwie. Zwrócono uwagę na prawne uwarunkowania gospodarki złożami i wydobytymi surowcami mineralnymi oraz bezpieczeństwo pracy i podejmowane działania w zakresie działalności badawczo-rozwojowej w sektorze.

Słowa kluczowe: surowce mineralne, zrównoważony rozwój, nakłady na działalność badawczo-rozwojową



The Role of Net Working Capital in the Financing of the Operating Activities of Mining Companies

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Abstract

The paper examines how companies' net working capital is used to finance their operating activities. Net working capital is a source of long-term financing (equity and long-term external capital) and is more expensive than financing through short-term sources, hence its rational use has a significant impact on the efficiency of companies' operations. The computed level of net working capital is used to calculate ratios enabling companies to control this capital. The ratios indicate the relationship of net working capital to current assets, to the sum of accounts receivable and short-term investments, to cash and cash equivalents, and sales revenues. Based on these calculations of the relationships, an assessment was made of net working capital engagement in the financing of operating activities in mining companies. These companies maintain a high degree of current asset financing through long-term capital. In mining companies. This is due to the maintenance of a higher level of inventories of extracted raw materials, the distance of outlets from the place of extraction and the method of transport used. Based on the ratio of net working capital to cash and cash equivalents, it was found that some companies were overly liquid. Cash balances significantly exceed the value of this capital over a period of three to four years. A surplus of cash over net working capital in the short term cannot be treated as excess liquidity, as it is the due to flexible management of this capital.

Keywords: net working capital, net working capital ratios, excess liquidity

Introduction

The dynamic environment in which companies operate and changes in the economic situation make the management of net working capital increasingly important. In the company's financing structure, net working capital is like the circulatory system in the human body. When managed effectively, it allows the company to remain financially healthy and competitive. When it is not afforded the attention it deserves, it leads to payment gridlocks and sometimes to bankruptcy (Skoczylas, 2015). Early identification of problems requires the company to have tools with which it can control changes in the level of net working capital relative to current needs. To determine whether the level of net working capital is rational, the ratio of this capital to total assets, current assets, total accounts receivables and short-term investments, cash and cash equivalents, and sales revenues is calculated. Besides accounts payable, net working capital is a source of financing of current assets. When its level is too low in relation to the needs, this leads to a loss of liquidity and an increase in cost of goods sold (COGS) in the form of penalty interest. An excessive level of working capital increases opportunity costs and the average cost of capital. This prompts companies to systematically monitor its level and rationally manage this capital.

The paper aims to present the results of research into the share of net working capital in the financing of operating activities in Polish and global mining companies. An attempt was made to verify the hypothesis predicting that Polish coal companies manage their net working capital more rationally than global companies. They do not keep an excessive level of working capital and do not generate opportunity costs.

The net working capital (NWC) affords the company a safety buffer that reduces the liquidity risk. It is more expensive than short-term capital, hence its size has an impact on the efficiency of the company's operations. Relevant literature presents two ways in which NWC is calculated - capital related, and assets related. Under the capital related approach, net working capital is the difference between the values of capital and long-term debt and non-current assets. Under the assets related approach, it is calculated as the difference between current assets and short-term liabilities. The formulas presented above indicate that the calculation of NWC requires the transformation of the accounting balance into an itemised balance. Capital and long-term debt consists of all sources of assets financing with a period of return in excess of the balance sheet year. Short-term liabilities include short-term provisions, accounts payable and short-term accruals with a maturity of up to one year. Non-current assets are the sum of fixed assets and trade receivables with a return period over 12 months. Current assets are those that can be converted into cash within less than the balance sheet year.

Net working capital may be positive, which means that the company finances all its fixed assets and a part of its current assets through capital and long-term debt. Negative net working capital values indicate a lack of full coverage of even fixed assets through non-current sources of financing. All current assets and part of the fixed assets are then financed through short-term financing sources. Lack of net working capital means that current assets are financed through shortterm sources and fixed assets through long-term financing sources. Positive net working capital is well received by the company's environment as it indicates that there is no risk of loss of liquidity (Szemraj, Czajkowska, 2020). It should be

Analysis of Pertinent Literature

Tab. 1. Share of net working capital in mining companies' current assets, 2015-2019. Source: own calculations based on financial statements of mining companies retrieved from a Reuters database

Company	2015	2016	2017	2018	2019
Anglo American PLC	57.6	47.6	49.7	48,6	48.0
Arch Resources Inc.	(383.0)	64.5	59.8	62.5	56.0
BHP Group PLC	30.3	46.0	60.2	47.2	30.9
Coal India Ltd.	56.6	37.0	26.9	33.8	42.0
JSW SA	(170)	2.3	36.1	(4.7)	(4.0)
LWB SA	36.9	14.1	(2.0)	4.8	49.6
Peabody Energy Corp.	-	51.6	43.2	45.8	39.6
Raspadskaya PAO	11.1	(45.5)	(1.5)	37.6	70.3
Rio Tinto PLC	34.2	37.8	39.9	47.6	35.7
Vale SA Brazilian	31.8	50.2	30.8	40.8	18.8
Whitehaven Coal Ltd.	18.2	22.9	28.6	(6.7)	20.1

Tab. 1. Udział kapitału obrotowego netto w aktywach obrotowych w spółkach górniczych w latach 2015-2019. Źródło: obliczenia własne na podstawie sprawozdań finansowych spółek górniczych zaczerpnięte z bazy Reuters

added that although positive levels of net working capital reduce this risk, to maintain them the company must refrain from actions that could bring it tangible benefits in the form of higher profitability (Fresand, 2012). For net working capital to be managed properly, it is imperative to determine its proper structure. It's may only be sourced from equity capital, only long-term external capital or a structure composed of both equity and long-term debt.

Neither too low nor too high a level of net working capital is beneficial for the company. A shortage of this capital leads to liquidity problems, and an excess may result in excess liquidity. In the latter case, the company has funds that it is not able to use effectively. (Nehrebecka, Białek- Jaworska, 2016). The reasons for this phenomenon can be both internal and external. Internal reasons are either related to errors made by managers or result from the liquidity management system in place. Systemic errors result from an overly conservative strategy of net working capital management, which makes excess liquidity a permanent phenomenon in the company. Another reason underlying errors in the management of net working capital in the company leading to temporary states of excess liquidity is non-implementation of mechanisms allowing for the harmonisation of the value of current assets and shortterm liabilities, the size and structure of which depend on factors related to the seasonality of operations. External reasons for the company's excess liquidity may be caused by one-off events e.g., related to the behaviour of business partners, or a relatively permanent change in the environment e.g., a reduction in market interest rates. However, the impact of external events on excess liquidity is not direct - the mere occurrence of any of the factors does not result in an excessive increase in free cash, provided that the company takes remedial measures. Therefore, external factors as stimuli of excess liquidity are tightly bound up with internal factors. The consequences for the company in the event of excess liquidity are limited to opportunity costs generated by unused funds. They often remain unnoticed either to external recipients of information or to company managers (Adamska 2016, Abbadi, 2013)). If excess liquidity persists, then it requires adjustments in the net working capital management strategy.

In practice, it is difficult to determine the optimum level of net working capital. It can only be said that companies enjoying ready access to short-term capital funding in the form of multi-purpose credit lines, factoring lines and large overdraft limits can afford to maintain low levels of net working capital. Net working capital may be boosted by increasing capital and long-term debt or releasing the capital tied up in the financing of fixed assets. Capital and long-term debt can be increased by limiting dividend pay-outs and increasing retained earnings, issuing shares and bonds, taking out additional long-term loans and borrowings, using financial leasing and other forms of long-term sources of funding. Fixed assets can be reduced by disposing of redundant fixed assets, selling buildings and leasing the necessary office space, leaseback of fixed assets, sale of financial instruments and limiting investments in this area (Sierpińska, Sierpińska-Sawicz, et al., 2019).

Net Working Capital Strategies

The choice of methods used in net working capital management depend on corporate strategy. The right strategy has a positive impact on the financial security of the company, its efficiency, competitiveness and financial performance (Andrew, Gallagher, 2007). G. Zimon (2016a) points out that errors in the management of net working capital are a common cause of bankruptcy. Therefore, company management is intent to look for solutions that ensure the company's liquidity and limit bankruptcy risk. In the management of net working capital, the solutions come down to rationalising the level of inventories and receivables and flexibly using short-term liabilities to finance the company's operating activities. A shortage of financing sources for these activities is supplemented with an appropriate level of net working capital. Systematic control of the level of net working capital reduces the costs of financing its acquisition.

Pertinent literature distinguishes three major strategies for managing net working capital: conservative, aggressive and moderate. By implementing a conservative strategy, the company's current assets exceed its short-term liabilities. It maintains a level of inventories which exceeds the industry average (Wędzki, 2003). Although inventories improve liquidity ratios, they also generate additional costs arising from their very maintenance. A prudent trade credit policy, manifesting itself through short invoice payment terms or demanding that new customers pay cash reduces overdue receivables (Sierpińska, 2020). It also leads to a lower than industry average level of receivables. Managers try to settle short-term liabilities in a timely manner; hence their level is relatively low. Current assets are largely financed through positive net working capital. A conservative working capital management strategy manifests itself in an extremely cautious approach to controlling current assets and sources of their financing. Managers refrain from measures that could threaten

Tab. 2. Ratio of net working capital to total receivables and cash in mining companies, 2015-2019. Source: own calculations based on financial statements of mining companies retrieved from a Reuters database

Tab. 2. Relacja kapitału obrotowego netto do sumy należności i środków pieniężnych w spółkach górniczych w latach 2015-2019. Źródło: obliczenia własne na podstawie sprawozdań finansowych spółek górniczych zaczerpnięte z bazy Reuters

Company	2015	2016	2017	2018	2019
Anglo American PLC	96.1	78.6	79.2	83.4	87.9
Arch Resources Inc.	(575.0)	98.0	82.6	87.4	86.6
BHP Group PLC	39.5	56.9	111.3	57.8	39.5
Coal India Ltd.	79.7	58.8	46.9	61.1	81.6
JSW SA	(313.2)	3.0	43.3	(6.2)	(7.4)
LWB SA	45.8	15.9	(2.3)	6.1	59.3
Peabody Energy Corp.	(1227.3)	80.2	60.4	62.3	60.2
Raspadskaya PAO	15.6	(63.6)	(2.0)	62.4	87.0
Rio Tinto PLC	48.0	52.4	53.4	61.5	48.4
Vale SA Brazilian	96.1	141.9	83.7	73.5	29.7
Whitehaven Coal Ltd.	31.2	34.7	47.6	12.4	35.4

the company's financial stability, in particular from incurring excessive liabilities to finance current assets.

An aggressive strategy involves keeping current assets and short-term liabilities at a similar level. The company does not use its net working capital to finance its operating activities. Inventories are kept below the industry average. As a result of an aggressive strategy of accounts receivable management, their level is higher than the industry average. The company applies long invoice payment terms and does not enforce strict security for receivables or limit trade credit availability for new contractors. Such a policy boosts sales and the acquisition of new markets. The extension of invoice payment terms though may result not only from the pursuit of an aggressive strategy, but also from the company's poor competitive edge or a need to liberalise its credit policy at a time when it is entering new markets or launching new products onto the market. An increase in total receivables is accompanied by an increase in overdue receivables and the costs of their collection. The increase in receivables is financed through an increase in short-term liabilities. However, if the increase in these liabilities is lower than the increase in receivables, the company should supplement its net working capital to reduce the liquidity risk.

In their business practice, companies try to follow a moderate strategy. They maintain a rational level of inventories to minimise related costs. Invoice payment terms map those granted by competitors. Companies try to reduce the risk of forfeiting their receivables by examining a buyer's financial standing and demanding security against their receivables. The moderate strategy is characterised by average balances of current assets and short-term liabilities. Consequently, both risk and profitability are moderate. "By deploying this type of strategy, the company tries to minimise the weaknesses of the conservative and aggressive strategies and maximise their advantages" (Zimoń, 2016b, p. 554). This means that a moderate working capital management strategy is a balancing act between aggressive and conservative approaches. With this method of working capital management, companies take greater risk when moulding the working capital structure than with the conservative strategy, but also one which is smaller than with an aggressive strategy. Individual working capital management strategies differ in terms of the scope of the spectrum of potential financial benefits and capital needs of the company (Szemraj, Czajkowska, 2020).

The correct determination of the working capital management strategy consists in developing an action plan that shows the possibilities of finding such financing that will satisfy the demand for working capital arising in the course of business activity, without running liquidity risk (Teofil-Kaczmarek, 2007). K. Kreczmańska-Gigol (2010) indicates that the primary goal of the strategy should be to optimise the capital structure of the company because other goals, such as minimising the risk of bankruptcy or maximising income are its resultants. The point of formulating a working capital management strategy arises from the need for long-term planning of activities aimed at (Szemraj, Czajkowska, 2020):

- raising funds to finance various areas of the company's activity,
- adjusting the level of assets to capital resources,
- maintaining the relationship between equity and external capital at a level that maximises the advantage of benefits over costs due to the capital structure,
- improving the coordination and monitoring of the way in which capital is spent,
- harmonisation of revenues and expenses.

Research Methods

The degree of financing of operating activities through net working capital was determined based on data taken from a Reuters database. Basic relationships based on net working capital were calculated.

- Net working capital was calculated as the difference between current assets and accounts payable determined based on data from the balance sheets of the companies surveyed. The calculated share of net working capital in current assets shows the extent to which these assets are financed through long-term sources, which are more expensive than short-term sources, hence an excessive share of net working capital in the financing of current assets is not beneficial for companies as it increases the average cost of capital. This may limit the scope of profitable investment projects. Some investment projects may have a rate of return below the average cost of capital raised to finance them.
- 2. The share of net working capital in the financing of receivables and cash is expressed as a ratio of this capital to the sum of receivables and cash and cash equivalents. These are liquid components of current assets. When they is financed excessively through net working capital, this indicates a lack of rational capital management.

Tab. 3. Ratio of short-term investments to net working capital 2015-2019. Source: own calculations based on financial statements of mining companies retrieved from a Reuters database

Tab. 3. Relacja inwestycji krótkoterminowych do kapitału obrotowego netto. Źródło: obliczenia własne na podstawie sprawozdań finansowych
spółek górniczych zaczerpnięte z bazy Reuters

Company	2015	2016	2017	2018	2019
Anglo American PLC	86.9	101.0	107.5	101.4	95.0
Arch Resources Inc.	(14.9)	69.4	86.4	77.8	72.9
BHP Group PLC	194.3	146.4	75.1	173.0	202.5
Coal India Ltd.	97.4	121.9	177.9	139.4	81.4
JSW SA	(13.8)	2052.6	182.4	-	-
LWB SA	110.6	441.0	(2918.8)	752.9	103.8
Peabody Energy Corp.	(4.3)	80.8	107.1	109.5	114.6
Raspadskaya PAO	154.8_	(11.8)	(500.0)	20.4	73.6
Rio Tinto PLC	181.6	149.9	155.7	139.4	172.2
Vale SA Brazilian	72.9	37.6	74.0	92.7	255.6
Whitehaven Coal Ltd.	195.4	190.4	100.7	(492.5)	140.3

- 3. The ratio of short-term investments (cash and cash equivalents) to net working capital is indicative of the extent to which long-term capital is involved in the financing of the most liquid current assets. When the value of this ratio exceeds 100 in the long term, this means that the company maintains temporary excess liquidity. A high level of financing of cash through long-term capital which persists over a long period of time may signal a low efficiency of capital use.
- 4. The ratio of net working capital to sales revenues indicates what level of net working capital is used to generate specific revenues. An increased burden placed on revenues in the form of net working capital requirement may deteriorate the profitability of sales.

Assessment of the Engagement of Net Working Capital in the Financing of Current Assets in Mining Companies

The share of net working capital in current assets in the surveyed companies presented in Table 1 indicates a relatively high involvement of long-term capital in the financing of operating activities. In the balance sheet, this is reflected in the level of inventories, receivables, short-term investments and short-term deferred charges and accruals.

At an average of 60% in 2016-2019, Arch Resources reported the highest level of financing of current assets through net working capital. At Anglo American and the BHP Group, the ratio reached 50%. In several companies, it amounted to 30%. Notably, in Polish coal companies it was very low. In the last two years of the period analysed, JSW SA reported negative net working capital indicating that accounts payable were used to finance part of the fixed assets. In Polish coal companies, the share of net working capital in current assets was highly volatile. In LWB, in 2017 negative net working capital accounted for 2.0% of current assets, and in 2019 almost 50% of these assets were financed through long-term capital. Similarly, in the Russian company Raspadskaya, 2017 saw a negative working capital, and in 2019 this capital financed 70% of current assets. The degree of current asset financing through long-term capital depends to a large extent on the level of maintained inventories of extracted raw materials. If a company extracts multiple raw materials, such as copper, iron ore, coal, molybdenum, cobalt, etc., and has distant sales markets, it must maintain a high level of inventories to ensure regular deliveries to customers. Companies such as Anglo American, BHP Group, Rio Tinto, and Vale SA have diverse activities. They have a more stable share of net working capital in the financing of current assets than companies mining only coal.

Table 2 shows the share of net working capital involved in the financing of receivables and cash and their equivalents. A high degree of this involvement may indicate an irrational use of long-term capital. Long-term capital is more expensive than the short-term one. It includes equity capital, the raising of which does not reduce the tax base. Dividends paid to shareholders are a direct cost arising from equity. Long-term external capital generates higher costs than short-term capital due to a higher risk premium, continuity of availability and security pledged. For example, long-term loans are secured by a mortgage or lien on movable property, while short-term loans are secured by an assignment of receivables or a bank or insurance guarantee.

The analysed coal companies reveal a high level of financing of liquid current assets through net working capital. It averages 60-80% and results from the level of free cash kept in accounts, as indicated by the data in Table 3. In Polish coal companies, the degree of liquid assets financing through net working capital is low and varies over time. Yet, the above does not validate the conclusion that net working capital is too low to finance receivables and short-term investments. To determine if correct sources of financing of operating activities were selected, attention should be paid to the structure of liquid assets and the share of cash in them. When a high share of cash in relation to net working capital persists in the long run, it is not good for the company.

By engaging long-term capital that makes up the net working capital, the company incurs the costs of its acquisition. Free cash however, even if invested in the short term, generates a much lower rate of return than the cost of raising capital. Therefore, the company incurs opportunity costs, i.e., the costs of frozen capital not invested in more profitable assets.

In general, companies should not use excess net working capital to finance operating activities if they hold surplus cash. They should maintain an optimum level of cash, which is a compromise between minimising the risk of insolvency and maximising the profit from long-term investments in their development. At Anglo-American, the level of cash and cash equivalents held is equal to net working capital. In 2019, cash at BHP was more than twice as high as its net working capital. In Polish mining companies, the levels of this ratio in selected years were exceptionally high. At the end of 2016, JSW SA held PLN 1,170 million in its account and its working capital Tab. 4. Ratio of net working capital to sales revenues in mining companies, 2015-2019. Source: own calculations based on financial statements of mining companies retrieved from a Reuters database

Tab. 4. Relacja kapitału obrotowego netto do przychodów ze sprzedaży w spółkach górniczych w latach 2015-2019. Źródło: obliczenia własne na podstawie sprawozdań finansowych spółek górniczych zaczerpnięte z bazy Reuters

Company	2015	2016	2017	2018	2019
Anglo American PLC	0.39	0.28	0.27	0.23	0.22
Arch Resources Inc.	(1.69)	0.29	0.21	0.22	0.17
BHP Group PLC	0.19	0.27	0.49	0.25	0.16
Coal India Ltd.	0.49	0.31	0.21	0.24	0.36
JSW SA	(0.37)	0.01	0,16	(0.02)	(0.02)
LWB SA	0.13	0.07	(0.08)	0.01	0.17
Peabody Energy Corp.	(1.07)	0.23	0,17	0.17	0.14
Raspadskaya PAO	0.07	(0.59)	(0.01)	0.30	0.78
Rio Tinto PLC	0.15	0.17	0,19	0.24	0.14
Vale SA Brazilian	0.25	0.39	0.18	0.18	0.09
Whitehaven Coal Ltd.	0.07	0.05	0.05	(0.01)	0.03

totalled a mere PLN 57 million. In 2018, cash amounted to PLN 1,651 million and negative working capital to PLN 164 million. The company did not finance its most liquid assets i.e., cash and cash equivalents through long-term capital. In 2018, LWB SA held PLN 171 million in its account and its working capital totalled a mere PLN 22.7 million, so cash was 7.5 times higher than its working capital. This indicates rational capital management under which even a small amount of cash held relative to a low level of working capital would indicate excess liquidity, hence the presented ratios must be viewed with caution. Only long-term cash balances significantly exceeding working capital may be indicative of excess liquidity. Such excess liquidity is visible in the ratio of cash to net working capital in BHP Group, Rio Tinto and Whitehaven Coal. It results from large fluctuations in the bottom line.

Assessment of the adequacy of net working capital management must not disregard the relation of this capital to sales revenues (Table 4). The ratio is highly volatile because of changes in specific net working capital management strategies. In the conditions of stiff competition, companies extend invoice payment terms inflating the level of receivables. Likewise, increasing the availability of products requires that the level of inventories be increased, which, in turn, necessitates the use of more capital and long-term debt to finance current assets. The lowest level of net working capital involvement in relation to revenues is reported by Polish coal companies. They do not maintain excessive stocks of coal. At JSW SA, the inventory cycle is 30 days, and at LWB SA it totals 20 days. In large corporations pursuing diverse activities, 1 PLN of revenue corresponds on average to PLN 0.20 net working capital. In coal companies, this ratio is more stable than in

coal companies. The use of net working capital to finance sales revenues is influenced by changes in the demand for coal and its prices.

Conclusions

Summing up, it should be emphasised that net working capital in the company serves to reduce the risk resulting from lower liquidity of some current assets (inventories, receivables) or from maturity dates of accounts payable. Net working capital is a financial cushion at the company's disposal at all times and can be used as a source of financing of operating activities. By using net working capital, the company bears the cost of capital. Hence, the involvement of this capital in operating activities must be balanced, on the one hand in terms of costs, and on the other, in terms of the company's debt servicing capacity. Too high a share of net working capital in the financing structure of current assets depresses the profitability of companies' activity. Meanwhile, a high share of net working capital in the financing of current assets is often the reason for a positive assessment of the company, especially by external stakeholders, who use it to weigh the risk of the company's insolvency. In mining companies, a high share of net working capital in the financing of current assets results from the need to maintain inventories of mined raw materials. Polish mining companies use net working capital to finance current assets to a much lesser extent than global companies. This confirms the hypothesis proposed in the research. In many global companies, a high ratio of net working capital to cash indicates excess liquidity. This signals to managers that they should change their strategy of net working capital management.

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Rola kapitału obrotowego netto w finansowaniu działalności operacyjnej spółek górniczych W artykule podjęto problem wykorzystania kapitału obrotowego netto do finansowania operacyjnej działalności przedsiębiorstw. Kapitał obrotowy netto to długoterminowe źródła finansowania (kapitał własny i obce kapitały długoterminowe) droższe od źródeł krótkoterminowych, stąd racjonalne ich wykorzystanie ma istotny wpływ na efektywność funkcjonowania przedsiębiorstwa. Ustalony poziom kapitału obrotowego netto jest podstawą konstrukcji wskaźników umożliwiających sterowanie tym kapitałem. Wskaźniki te to relacje kapitału obrotowego netto do aktywów obrotowych, do sumy należności i inwestycji krótkoterminowych, do środków pieniężnych i ich ekwiwalentów oraz przychodów ze sprzedaży. W oparciu o tak obliczone relacje dokonano oceny zaangażowania kapitału obrotowego netto do finansowania operacyjnej działalności spółek górniczych. Spółki te utrzymują wysoki stopień finansowania aktywów obrotowych kapitałami długoterminowymi. W spółkach górniczych o zdywersyfikowanej działalności wydobywczej poziom finansowania aktywów obrotowych kapitałem długoterminowym jest wyższy niż w spółkach wydobywających wegiel. Jest to wynikiem utrzymywania wyższego poziomu zapasów wydobywanych surowców, odległości rynków zbytu od miejsca wydobycia oraz rodzaju wykorzystywanego transportu. Na podstawie relacji kapitału obrotowego netto do środków pieniężnych i ich ekwiwalentów ustalono, że w niektórych spółkach występuje nadpłynność finansowa. Środki pieniężne są znacznie wyższe niż ten kapitał w okresie trzech – czterech lat. Nadwyżka środków pieniężnych nad kapitałem obrotowym netto w krótkim okresie nie może być traktowana jako nadpłynność finansowa, gdyż jest wynikiem elastycznego zarządzania tym kapitałem.

Słowa kluczowe: kapitał obrotowy netto, relacje oparte na kapitale obrotowym netto, nadpłynność finansowa



A Study of PM 10, PM 2.5 Concentrations in the Atmospheric Air in Kraków, Poland

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Abstract

The air in Kraków is one of the most polluted in Europe. Polish standards for notification and alert levels for PM10 particulate matter are one of the the highest in Europe and exceed the recommendations of the World Health Organization (WHO) for safe daily concentrations by several times. The article presents the results of airborne dust measurements in three districts of Kraków. The study has shown that the concentration of PM2.5 and PM10 particulate matter exceeded the annual average permissible levels. Empirical measurements of PM2.5 show significantly higher air pollution values than the data notified by stationary monitoring stations installed in two locations. The high value of Pearson linear correlation coefficient confirms that weather conditions have a significant impact on air quality in Kraków. Wind speed in the autumn and winter seasons has by far the greatest influence on air quality in al. Krasińskiego, in the Ruczaj and Kurdwanów districts. A strong negative correlation was displayed. Manual measurements should be used to verify data obtained from air monitoring stations. It is to be expected that, in Kraków, air purity will improve due to the implementation of an anti-smog resolution and subsidies for the replacement of obsolete heating systems with more environmentally friendly solutions.

Keywords: particulate matter, air quality, pollution, Kraków

Introduction

In the 21st century, the problem of human pressure on the environment has become a major issue. As a result of population growth, urbanization, industrial development and communication boost, the demand for energy and natural resources has increased. This has caused the growing concentration of pollutants introduced into the natural environment, especially into the air. The increase in the emission of pollutants from anthropogenic sources has forced national and international authorities to adopt stringent regulations. Through environmental monitoring, the society can stay informed about any threats emerging when the airborne pollutant standards are being surpassed.

Commission Directive (EU) 2015/1480 of 28 August 2015 amending several annexes to Directives 2004/107/EC and 2008/50/EC of the European Parliament and of the Council, laying down the rules concerning reference methods, data validation and location of sampling points for the assessment of ambient air quality, is an important document regulating low-stack emissions [1]. Suspended particulate matter was included in the group of pollutants with harmful effect on human health. It was agreed that information on the state of air quality must be available to the public.

In Poland, the basic legal act pertaining to air quality is the Act of 27 April 2001 Environmental Protection Law [2]. The law defines the principles of using the environment and protecting its components. Air protection programs aim to improve air quality and achieve specific levels of concentration of harmful substances. The Environmental Protection Law has been amended several times, for example the Act of 10 September 2015 [3] gives the provincial assemblies the possibility to introduce restrictions and bans on the operation of heating installations, in particular furnaces, boilers and fireplaces where solid fuels are burned. This applies to installations supplying heat to a central heating systems or directly releasing heat [2].

Under the amended Environmental Protection Law, the Małopolska Region Assembly adopted Resolution No. XXXII/452/17 of 23 January 2017 on the introduction of restrictions and bans on the operation of installations in which fuels are burned, the so-called antismog resolution [4]. For Kraków, it stipulated a ban on the use of poor quality solid fuels from July 1, 2019 to August 31, 2019. The limitation concerned biomass with humidity exceeding 20% and coal with grain size up to 5 mm constituting 5% of fuel, ash content above 10%, sulfur content above 8% and calorific value below 26 MJ/kg. In turn, as of September 1, 2019, a total ban on burning solid fuels in stoves, boilers and fireplaces has been in effect in Kraków. The only permissible fuels are natural gas or light fuel oil. Moreover, it is forbidden to smoke bonfires and use stationary barbecues [5].

With regard to energy efficiency, the European regulations have been implemented into Polish law by the Energy Efficiency Act of 20 May 2016 (Journal of Laws of 2016 item 831) [6]. Municipalities and local authorities are obligated to apply at least one solution improving energy efficiency. Examples of such measures are: investments in new installations and equipment, modernization of old installations, implementation of the EMAS environmental management system [2].

Particulate matter concentration standards

The permissible level, or air quality standard [7], is the concentration of a substance that can be reached in a given period of time and should not be exceeded after that time.

Name of substance	Averaging period	Permissible level in the air in 2020 [µg/m³]	Permissible annual frequency of exceeding the level
particulate matter PM 2.5	Calendar year	20	-
particulate matter	24 hours	50	35 times
PM10	Calendar year	40	-
PM10	Calendar year	40	





Fig. 1. Location of measurement points (Kraków. 1- al. Krasińskiego, 2- Ruczaj, 3- Kurdwanów) [13] Fig. 1. Lokalizacja punktów pomiarowych (Kraków. 1- aleja Krasińskiego, 2- Ruczaj, 3- Kurdwanów) [13]

The information level is the level of the substance in the air above which there is a risk to human health from brief exposure to pollutants of vulnerable population groups. The information level for PM2.5 is 150 μ g/m³, the averaging period is 24 hours, the information level for PM10 is 100 μ g/m³, the averaging period is 24 hours [8]. The alarm level is the concentration of a substance in the air which, if exceeded in the short term, could cause a hazard to human health [9,10,11].

The admissible concentration standards are the same throughout the European Union, but the notification and alarm levels are treated individually, as their values are not specified in the laws. In a controversial approach, the Polish 24-hour standards for PM10: notification (100 μ g/m³) and alarming (150 μ g/m³) are the highest in Europe. Alarming standards exceed the recommendations of the World Health Organization (WHO) for safe daily concentrations [12] by three times.

Methodology and Experimentals

The study was conducted in three stations located in Kraków (fig. 1): on the border of district I Stare Miasto and VII Zwierzyniec, as well as in districts VIII Dębniki and XI Podgórze Duchackie. The choice of location of measuring points was determined by two factors:

- the presence of measuring stations of the Voivodeship Inspectorate for Environmental Protection in Kraków in the case of the location of stations no. 1 in aleja Zygmunta Krasińskiego and no. 3 Kurdwanów, in order to compare the results;
- the absence of a measuring station in the Ruczaj area (station no. 2), to inform the residents and students of the Jagiellonian University about the particulate matter levels.

The research was conducted from July 23, 2018 to March 6, 2019. The WP6130 dust meter, equipped with PM10 and PM2.5 particulate matter concentration (in the range of 0-999 μ g/m³), air temperature and humidity detectors was used as the measurement tool. The device is equipped with airborne

formaldehyde and volatile organic compound concentration detectors. Measurements were taken once a day in real time and then were compared with measurements for a 24-hour averaging time. Readings were taken after the results were stabilized 20 seconds after the device was turned on.

At the same time, meteorological data was taken from the AccuWeather online platform for individual measuring stations [14]. The data consisted of the following parameters: PM 2.5 and PM 10 particulate matter, cloudiness, relative humidity, air temperature, wind speed and direction, precipitation and atmospheric pressure.

The measurements of concentrations of PM2.5 and PM10 particulate matter in al. Krasińskiego in Kraków were taken in the following periods:

- in the summer: from July 23, 2018 to September 18, 2018;
- in the autumn: from September 26, 2018 to October 26, 2018 (Fig. 2);
- in the winter: from January 18, 2019 to March 06, 2019 (Fig. 2).

The highest dust concentration was recorded on February 1, 2019, when PM2.5 was 146 $\mu g/m^3$ and PM10 was 163 $\mu g/m^3.$ The lowest concentration was recorded on October 24, 2018, when: PM2.5 was 5 µg/m3 and PM10 was 7 µg/m3. In addition, the weather conditions for the current measurement hour are marked. Cloudiness ranged from: 0% to 88% in the summer, from 9% to 90% in autumn, from 0% to 98% in the winter. According to the weather forecast, relative humidity oscillated between 42% and 84% in the summer, between 42% and 77% in autumn, between 36% and 99% in the winter. According to the weather forecast, air temperature was: from 19°C to 30°C in the summer, from 8°C to 21°C in autumn, from -6°C to 17°C in winter. Wind speed was: 4-20 km/h in the summer, 7-41 km/h in autumn, and 4-43 km/h in the winter. Precipitation of maximum 2 mm was recorded on three days only. Atmospheric pressure ranged from 101.00 kPa to 102.40 kPa in the summer, from 100.50 kPa to 103.60 kPa in autumn, and from 100.00 kPa to 103.30 kPa in the winter.



Fig. 2. Graphic illustration of PM10 and wind speed measurements – autumn. Al. Krasińskiego in Krakow Fig. 2. Ilustracja graficzna wyników pomiarów PM10 i prędkości wiatru - jesień. Aleja Krasińskiego w Krakowie



Fig. 3. Graphic illustration of PM10 and wind speed measurements – winter. Al. Krasińskiego in Krakow Fig. 3. Ilustracja graficzna wyników pomiarów PM10 i prędkości wiatru - zima. Aleja Krasińskiego w Krakowie

At the monitoring station in al. Krasińskiego, the permissible PM10 particulate matter concentration was exceeded 21 times, reporting the value of 50 μ g/m3 in a 24-hour standardized result period, whereas in Kurdwanów, this level was exceeded 15 times [15, 16]. Comparing the PM2.5 readings taken by the dust meter and by the monitoring station, it may be claimed that both in al. Krasińskiego and in Kurdwanów, the dust meter showed significantly higher contamination. In the case of PM10 particulate matter, the difference between dust meter measurements and monitoring station measurements is not statistically significant and may result from measurement error.

Results

The Pearson linear correlation coefficient (rxy) [17], applied in the study of the straight-line correlation between two variables of normal or symmetrical distribution, was used in the study. The calculated Pearson correlation coefficient for the parameters measured in al. Krasińskiego in Kraków is presented in table 2.

In summer, a moderate positive correlation was identified between particulate matter concentrations and relative air humidity (0.51), as well as a weak positive correlation between particulate matter concentration and atmospheric pressure (0.36). Moreover, a moderate negative correlation between air temperature and particulate matter concentration was noted (-0.55). In autumn, a moderate negative correlation was found between cloudiness (-0.57) and particulate matter concentration, and a strong negative correlation between wind speed (-0.63) and particulate matter concentration. In addition, there is a moderate positive correlation between air temperature and particulate matter concentration (0.51). In the winter, a moderate negative correlation between wind speed and particulate matter concentration between wind speed and particulate matter concentration was noted (-0.41).

Table 3 presents the rxy coefficient for the values of the parameters recorded in Ruczaj in Kraków.

In summer, a moderate positive correlation was identified between particulate matter concentrations and relative air humidity (0.50), as well as a moderate negative correlation between particulate matter concentration and air temperature (-0.45). In the autumn, a strong negative correlation between wind speed and particulate matter concentration can be seen (-0.77), as well as a strong negative correlation between cloudiness and particulate matter concentration (-0.62). Furthermore, there was a moderate positive correlation between air temperature and particulate matter concentration (0.53). In the winter, a weak negative correlation between wind speed and particulate matter concentration (-0.39) was observed.

Table 4 presents Pearson correlation coefficients obtained for values of particular parameters in Kurdwanów.

In the summer period, a weak positive correlation between particulate matter concentration and relative air humidity (0.35) and a weak negative correlation between particulate matter concentration and air temperature (-0.35) were recorded. In autumn, on the other hand, a weak positive correlation was reported between particulate matter concentration and relative air humidity (0.36) and a weak positive correlation between particulate matter concentration and air temperature (0.38). In addition, there was a strong negative correlation between particulate matter concentration and wind speed (-0.68), and a moderate negative correlation between particulate matter concentration and cloudiness (-0.44). In the winter, a moderate negative correlation between particulate matter concentration and wind speed can be seen (-0.55) and a weak negative correlation between particulate matter concentration and cloudiness (-0.35).

Disscussion

Pro-environmental activities depend on local government bodies. The methods of preventing dust emission are associated with legal as well as technical and organizational lim-

Cloudy Humidity Temperature Wind speed Air pressure -0,04 PM2.5 0.51 -0.55 -0.12 0.36 Summer PM10 -0.05 0.52 -0.12 -0.54 0.36 PM2.5 -0.57 0.29 0.51 -0.63 0.26 Autumn PM10 **-**0,57 0.29 0,51 -0,63 0.25 PM2.5 -0.25 0.18 -0,16 -0,40 -0.02 Winter PM10 **-**0,25 0,18 -0,16 -0,41 -0,03

Tab. 2. Pearson's correlation coefficients for the values of individual parameters. Al. Krasińskiego in Krakow Tab. 2. Współczynniki korelacji Pearsona dla wartości poszczególnych parametrów przy al. Krasińskiego w Krakowie

Tab. 3. Pearson's correlation coefficients for the values of individual parameters. Ruczaj Tab. 3. Współczynniki korelacji Pearsona dla wartości poszczególnych parametrów. Ruczaj

		Cloudy	Humidity	Temperature	Wind speed	Air pressure
Summer	PM2.5	0,22	0,50	-0,45	0,02	0,18
	PM10	0,19	0,47	-0,43	0,01	0,18
Autumn	PM2.5	-0,62	0,01	0,53	-0,77	0,21
	PM10	-0,62	0,01	0,53	-0,77	0,21
Winter	PM2.5	-0,27	0,18	-0,09	-0,39	-0,06
	PM10	-0,27	0,18	-0,09	-0,39	-0,07

Tab. 4. Pearson's correlation coefficients for the values of individual parameters. Kurdwanów Tab. 4. Współczynniki korelacji Pearsona dla wartości poszczególnych parametrów. Kurdwanów

		Cloudy	Humidity	Temperature	Wind speed	Air pressure
Summer	PM2.5	0,27	0,35	-0,35	-0,17	0,10
	PM10	0,28	0,33	-0,33	-0,14	0,08
Autumn	PM2.5	-0,44	0,36	0,38	-0,68	0,26
	PM10	-0,44	0,36	0,38	-0,67	0,26
Winter	PM2.5	- 0,35	0,15	-0,05	-0,55	0,16
	PM10	- 0,37	0,12	-0,04	-0,54	0,13

itations [18]. As mentioned earlier, the principles of airborne particulate matter reduction are specified in the Environmental Protection Law. Due to the lack of definition of low-stack emissions, municipalities and local governments have been arbitrarily implementing Low-Stack Emission Reduction Programs. The restrictions and bans on burning solid fuels in the process of heat production proved to be an example of primary actions [2]. Due to these limitations, residents of Kraków have receive grants for the replacement of inefficient solid-fuel stoves with more environmentally friendly heating solutions, e.g. gas, electric, oil or municipal heating systems. The program is also based on the use of renewable energy sources in the heating industry: heat pumps and solar thermal collectors [10, 18]. As part of secondary activities limiting the emission of pollutants, buildings undergo thermal modernization in order to limit energy losses. It consists of thermal insulation of building partitions, as well as replacement of windows and doors with elements of appropriate technical parameters, while maintaining proper installation. Other important measures involve changing the heating source, ventilation systems and selecting correct stack parameters [2]. Dedusting systems which remove pollutants from flue gases also play an important role. Since transport is an important source of dust, a European emission standard has been introduced, which classifies vehicles according to the amount of pollutants emitted [16]. Another important pro-ecological action in transport is the expansion of public transport. Public buses use specially designated lanes, which allows them to travel several times faster in a crowded city. It should be noted that as part of its pro-ecological activities, the Municipal Tranportation Company in Kraków has 26 purchased low-emission electric buses manufactured by Solaris to run on its routes [19].

Conclusions

The analysis presented in the paper leads to the following conclusions:

- Weather has a significant impact on air quality, as confirmed by the high value of the Pearson linear correlation coefficient.
- Wind speed in the autumn and winter seasons has by far the greatest influence on air quality in al. Krasińskiego, in the Ruczaj and Kurdwanów dis-

tricts. A strong negative correlation and a moderate negative correlation were displayed.

- In all districts, a moderate negative correlation or a strong negative correlation between particulate matter concentration and cloudiness were recorded in autumn.
- In the summer, a moderate negative correlation and a weak negative correlation between particulate matter concentration and air temperature were observed in all districts, which then changed into a moderate positive correlation and a weak positive correlation in autumn.
- For the summer period, a moderate positive correlation was observed between air humidity and particulate matter concentration in al. Krasińskiego and in Ruczaj.

The air in Kraków is one of the most polluted in Europe, which was confirmed by measurements taken by monitoring stations: in al. Krasińskiego, in Ruczaj and in Kurdwanów, where the average annual PM2.5 and PM10 particulate matter exceeded the permissible annual levels.

In connection with the current ban on burning solid fuels in Krakow, the so-called anti-smog resolution, and subsidies for the replacement of obsolete heating with more environmentally friendly solutions, the situation is slowly improving. However, the inflow of pollution from the suburban areas, to which this ban does not apply, still creates significant nuisance for the agglomeration. The location of Kraków in a basin and the high level of air corridors [15], which further hinder ventilation, only strengthen the underlying issue. Air pollution causes a number of negative health effects within the society [20, 21, 22]. The most vulnerable groups are sick people, children, pregnant women and the elderly [23, 24]. Nation-wide environmental education and increasing the level of environmental awareness among the residents of Kraków are key to achieving the goal of reducing air pollution. Environmental action consist of both preventive and remedial measures.

Author Contributions:

Maciej Ciepiela did the data collection, wrote the paper and result analysis. Wiktoria Sobczyk conceived, designed the search, wrote the paper and result analysis. Both authors have read and approved the final manuscript.

Conflict of interest statement

The authors declare no conflict of interest.

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Badanie stężeń PM 10, PM 2,5. w powietrzu atmosferycznym w Krakowie, Polska

Krakowskie powietrze jest jednym z najbardziej zanieczyszczonych w Europie. Polskie normy poziomów informowania oraz alarmowego dla pyłu zawieszonego PM10 są najwyższe w Europie i kilkakrotnie przekraczają zalecenia Światowej Organizacji Zdrowia (WHO) w odniesieniu do bezpiecznych stężeń dobowych. W artykule przedstawiono wyniki pomiarów zapylenia powietrza w trzech dzielnicach Krakowa. Badania wykazały, że stężenie pyłów zawieszonych PM2.5 i PM10 przekroczyły średnioroczne poziomy dopuszczalne. Pomiary empiryczne PM2.5 przedstawiają znacznie wyższe wartości zanieczyszczenia niż dane ze stacjonarnych stacji monitoringu na dwóch stanowiskach. Wysoka wartość współczynnika korelacji liniowej Pearsona potwierdza, że warunki pogodowe mają istotny wpływ na jakość powietrza w Krakowie. Zdecydowanie największy wpływ na jakość powietrza ma prędkość wiatru w okresach: jesiennym i zimowym na al. Krasińskiego, na Ruczaju i na Kurdwanowie. Wykazano znaczącą odwrotną zależność. Pomiary manualne należy stosować w charakterze weryfikacji danych ze stacji monitoringu powietrza. Należy się spodziewać, że na terenie Krakowa czystość powietrza będzie się poprawiać w związku z obowiązującą uchwałą antysmogową oraz dotacjami na wymianę ogrzewania na bardziej przyjazne środowisku.

Słowa kluczowe: cząstki pyłowe, jakość powietrza, zanieczyszczenie, Kraków



Stochastic Simulation of Production Processes – Selected Issues

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Abstract

The article presents selected issues in the field of stochastic simulation of production process-es. Attention was drawn to the possibility of including, in this type of models, the risk accompany-ing the implementation of processes. Probability density functions that can be used to characterize random variables present in the model are presented. The possibility of making mistakes while creat-ing this type of models was pointed out. Two selected examples of the use of stochastic simulation in the analysis of production processes on the example of the mining process are presented.

Keywords: stochastic simulation, production process, probability density function

1 Introduction

According to generally adopted definitions (e.g. Robinson 2004), to simulate means to mimic or imitate a real system by means of experiments conducted on a model representing (presenting) that system.

Simulation, however, is not just about imitation and experimentation. It also assumes defin-ing, designing, and building a model, as well as defining the experiments that will be run and col-lecting and analyzing the data needed to run the model along with analyzing and interpreting the results obtained from the experiments.

People all over the world are currently in a constant search for ways to reduce costs and make optimal use of resources. Achieving this in a dynamic, complex and interconnected global environ-ment is undoubtedly a challenge. Organizations are looking for lean system solutions to slim down their operations by eliminating everything that does not bring value to the customer while stream-lining the manufacturing process. They prepare value stream maps, identifying where time wasters and human effort occur. Optimization is treated as a key to success today (Beaverstock et. al. 2012).

Managers who make decisions in organizations need to know what is happening in their sys-tems, as well as what will happen in their systems and what actions need to be taken against those changes. A basic definition of a system characterizes it as a collection of interrelated elements with-in defined boundaries (Checkland 1981). In practice, the system can be very elaborate and represent a factory or organization, or quite simple, when it characterizes a workstation, an emergency room in a hospital, or a service desk at a bank. Decision-making is easy in simple systems and in situations with limited choice. However, more complex systems usually offer a large number of options for action.

Analyzing and making the right decision in the course of a manufacturing process is difficult because each system has one or more features, the general characteristics of which are as follows (Beaverstock et. al. 2012):

- 1. System components may be subject to random events.
- 2. Ambient random events affect the system.
- 3. The behavior of the system is dependent on an essential variable - time.
- 4. System elements encompass many interactions, and therefore there are many ways to con-nect paths between system elements.

Random events are common in manufacturing systems. These can include machine failures, operator response time to an incident, material delivery time and material losses, etc. When a man-ager proceeds to analyzing a system and formulates a plan to optimize its performance, they may encounter extremely difficult problems. Traditional analytical methods may not be sufficient in view of the dynamic and random nature of the system's behavior. Therefore, methods have been devel-oped to help managers analyze processes and are commonly known as decision support systems (Beaverstock et. al. 2012).

A decision support system applies analysis tools to help the decision maker formulate action plans. Simulation is one of them. Simulation (Robinson 2004) is defined as experimentation and simplified imitation (computer-assisted) of a specific action. It provides mechanisms for exploring the system presented in it, alternatively experimenting and predicting the outcome of proposed ex-ternal solutions. This approach significantly increases the decision space (allows for evaluating a greater number of different ideas), does not interfere with the actual system, and allows for estimat-ing the risk of actions. Managerial activities will be more effective if simulation modeling applica-tions are embedded in decision support systems, as this facilitates data entry into the model and improves the presentation of the resulting model.





2 Stochastic simulation

In this paper, special emphasis is placed on stochastic simulation. This method is used for computer modeling of any processes (physical, economic, technological, etc.) or their fragments, whose characteristic feature is the presence of at least one random variable in their description.

The method was first used during the Manhattan Project research to build the U.S. atomic bomb. The stochastic model developed at that time concerned the analysis of neutron propagation in a nuclear reactor. It was developed jointly by John von Neumann and Stanisław Ulam, a Polish mathematician.

The stochastic simulation method has been successfully used until today. The possibilities of creating complex stochastic models, their recording in the form of a computer program in a language oriented at solving this type of problems, as well as the constantly improving capabilities of comput-ers, all determine the choice of stochastic simulation as a method of solving problems described by models of an undetermined nature.

The current state of development of computer technology makes it possible to create accurate mathematical and economic models that can be used in decision-making processes applicable to programming, design and production planning.

Computational methods referred to as Monte Carlo are closely related to stochastic simula-tions. They involve using "artificially generated" randomness to solve deterministic tasks. Monte Carlo methods are relatively simple and efficient, and, for some problems, they are the only compu-tational tool available. Stochastic simulations are available to everyone due to the availability of free and open source software that allows any computer user to use such tools. As an example, the R language is a powerful tool (see Niemiro 2013).

The literature is very extensive, and one can mention works in the field of random number generators (e.g. Zielinski, Wieczorkowski 1997), and a monograph (Ripley 1987) which also includes an introduction to the Monte Carlo methods. Advanced lectures can be found in modern mono-graphs by Asmussen and Glynn (Asmussen, Glynn 2007), Liu (Liu 2004), Robert and Casella (Rob-ert, Casella 2004). The former is more oriented towards theoretical results, while the latter is more oriented towards applications. An introduction to Markov Chain Monte Carlo methods is included in the work of Geyer (Geyer 1992, Geyer 2005). The Markov chain theory with issues relevant to Mar-kov Chain Monte Carlo is also presented by Brémaud (Brémaud 1999). The theoretical basis for the analysis of randomized algorithms can be found in the work of Jerrum and Sinclair (Jerrum, Sinclair 1996) and Jerrum (Jerrum 1998), among others.

The use of stochastic simulation - as a research method - can be accompanied by errors or in-accuracies, which are illustrated in Figure 1. Individual terms mean: a real process is a process that is being studied by a simulation method; a model is a set of equations, inequalities, and/or algorithms that have been adopted as a mathematical description of the real process; a computer program is a notation of the model in a programming language of choice. Apparently minor mistake - made at the stage of building a model, writing it in the form of a computer program, or its verification - can be costly in its consequences. An analysis of such activities is presented in (Snopkowski 2009).

3 Distributions used in process description

Random variables occurring in process models (including for manufacturing processes) are characterized by appropriate probability density functions. What is also noteworthy, the existing functional relationships between random variables can be replaced by a single probability density function (the so-called result distribution), which causes that the developed stochastic model of the analyzed process is simplified (Snopkowski 2005a, Snopkowski 2005b).

Examples of probability density functions used in simulation models are summarized in Table 1.

4 Use of simulation in the analysis of manufacturing processes

Making decisions concerning business activity in the environment of market economy requires the manager to

lab. 1. Zestawienie funkcji gęstości prawdopodobieństwa stosowanych w symulacji stochastycznej. Żródło: opracowanie na podstawie Snopkowski 2005a, Snopkowski 2005b Tab. 1. Summary of probability density functions used in stochastic simulation. Source: compiled on the basis of Snopkowski 2005a, Snopkowski 2005b



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 to describe the time between successive floods;
 In mass service theory, it is the distribution of time intervals between requests;
 in reliability theory - to describe the time elapsed between vehicles for describing random variables that are more This distribution can be a characteristic of a ran-dom variable that is the square of another ran-dom variable with a t-Student distribution. - to describe the time taken to perform a specific - as a model for describing the strength of asikely than normal variables to take on abnormal values which deviate from the mean (t-Student distribution has thicker "tails"). Application examples passing a specific point on the road; Examples of applications include: Exponential distribution is used: operation on a machine tool; Tab. 1. Zestawienie funkcji gęstości prawdopodobieństwa stosowanych w symulacji stochastycznej. Żródło: opracowanie na podstawie Snopkowski 2005a, Snopkowski 2005b sembly structures; Tab. 1. Summary of probability density functions used in stochastic simulation. Source: compiled on the basis of Snopkowski 2005a, Snopkowski 2005b Diagram 3 8 0.4 0.3 0,2 5 2 6.0 0.6 0.3 5 1.0 0,5 8 2 $\left|\frac{\Gamma\left(\frac{n_{1}+n_{2}}{2}\right)}{\Gamma\left(\frac{k_{1}}{2}\right)\Gamma\left(\frac{k_{2}}{2}\right)}\frac{k_{1}}{k_{2}}\right|^{\frac{k_{1}}{2}}f^{\frac{k_{1}-2}{2}}\left(1+\frac{k_{1}}{k_{2}}f\right)^{-\frac{k_{1}+k_{2}}{2}}dla\,f>0$ λ - damage intensity, mean time between events ($\lambda > 0$) for a random variable of the *T*form $T = \frac{\sqrt{n-1}}{s} (\vec{X} - \mu)$ $dla f \leq 0$ Formula for the probability S - standard deviation of the sequence $\{X_n\}$ k - number of degrees of freedom (k=n-1)distribution function $f(x) = \begin{cases} \lambda e^{-\lambda x} & dla \ x > 0 \\ 0 & dlax \le 0 \end{cases}$ $f(\mathbf{c}) =$ $h(f) = \langle$ where: where: Exponential dis-tribution F-Snedecor distribution distribution **F**-Student Name

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demonstrate knowledge of many issues concerning the functioning of the company and its environment. Decision making is therefore burdened with high risk. To reduce the risk of possible failure of the decision made, many different types of risk assessment methods can be used to minimize the impact of adverse aspects of both the environment and internal business conditions.

A special case of using stochastic simulation is the simulation of a mining process, in which several stages can be distinguished. The first is to determine and systematize the set of input data and to develop a mathematical model, then to determine the probability distribution of random variables and to implement the simulation of the process and finally to analyze the simulation results obtained. Among the data necessary for the simulation are geological-mining, technical-organizational and financial data.

4.2 Identifying the probability distribution of extraction

A method of identifying the probability distribution of extraction (obtained from a longwall face) is an example of the possibility of using stochastic simulation in the analysis of a production process.

The output obtained depends on the number of cuts made by the shearer during the working shift. This relationship is described by the following formula:

$$Q_z = w_c \cdot T_d / T_c \tag{1}$$

where:

Q_z – extraction per shift [Mg/shift] w_c – output from a production cycle [Mg/zm].

 T_d – shift availability time [min/zm]

T_c – production cycle time [min/cycle]

Production cycle output is calculated according to the formula:

(2)

(4)

where:

w_=

l – length of the longwall face [m],

- h height of the longwall face [m],
- z production cycle take-up [m],
- γ volumetric coal weight [Mg/m³].

The production from the production cycle w_c for given geological parameters of the face is a constant quantity. The quotient T_d i T_c , on the other hand, determines the number of production cycles that are performed during a work shift, i.e:

$$L_c = T_d / T_c \tag{3}$$

Variables T_d and T_c have a direct impact on the level of extraction, and are also random variables because their values cannot be predicted with certainty before each work shift. Formula in (1) defines the relationship between three random variables, i.e. Q_s , T_d i T_c .

The identification of an extraction probability distribution occurs when its probability density function is determined. In doing so, one can use the well-known theorem:

Theorem 1. If X is a continuous random variable with density centered on an interval (a,b) and y=g(x), and is a strictly monotonic function of the C¹class with derivative on $g' \neq 0$ that interval while x=h(y) being the inverse of y=g(x), then the density k of the continuous random variable Y=g(x) is oin the form of

$$k(y) = f[h(y)]|h'(y)|$$

Fig. 3. Schematic diagram of calculation of output stream intensity index for a two-way shearer cutting technology Rys. 3. Schemat ideowy obliczania wskaźnika natężenia strugi wyjściowej dla technologii cięcia kombajnem dwukierunkowym



For c < y < d, for the remaining y function , k(y) = 0 where $c = min(c_1, d_1) d = max(c_1, d_1), c_1 = (lim)_{(x > a + 0)}g(x)cd_1 = (lim)_{(x > b - 0)}g(x).$

Identification of the probability distribution for extraction consists in obtaining the probability density function for a random variable Q_z defined by the relation

$$Q_z = w_c \cdot L_c \tag{5}$$

which is a strictly monotonic linear (increasing) function and satisfies the assumptions of Theorem 1.

The inverse of this function is the $L_c=(1/w_c)Q_z$ function , and its derivative is $L_c'=1/w_c$. Furthermore, it should be noted that output per cycle w_c is always greater than zero, so by Theorem 1, the probability density function of the random variable Q_z can be written as:

$$f_{q_z}(q_z) = \frac{1}{w_c} \cdot f_{l_c}\left(\frac{q_z}{w_c}\right) \qquad for \ q_z \in \mathbb{R}^+$$
(6)

where:

 $f_{\rm qz}(q_{\rm z})$ – probability density function of a random variable $Q_{\rm z}$ of mining per shaft,

 $f_{L_c}(q_z/w_c)$ – probability density function of the variable L_c of

number of production cycles per work shift.

As the variable L_c can also be represented by equation (3) then its probability density function f_{lc} can be determined using the following theorem:

Theorem 2. If random variable U is the quotient of random variables X and Y i.e. U=X/Y, then the quotient density of k_1 random variables X, Y is given by the formula

$$k_1(u) = \int_{-\infty}^{\infty} f(uy, y) |y| \, dy \tag{7}$$

and when X and Y are independent random variables with densities f, and f, then

$$k_1(u) = \int_{-\infty}^{\infty} f_1(uy) f_2(y) |y| \, dy$$
(8)

If we assume that the independent random variables T_d and T_c are characterized by the following probability density functions and respectively, f_{tc} (t_c) f_{td} (t_d)then based on equation (8), the probability density function of the random variable L_c represented by equation (3) is calculated according to the following equation:



Fig. 4. Empirical probability distribution of the output flow rate φ_{2k} Rys. 4. Empiryczny rozkład prawdopodobieństwa natężenia przepływu wyjściowego φ_{2k}



Fig. 5. Empirical distribution of the output flow rate Rys. 5. Rozkład empiryczny natężenia przepływu wyjściowego

$$f_{lc}(l_c) = \int_{-\infty}^{\infty} f_{td}(l_c t_c) f_{tc}(t_c) |t_c| dt_c$$
(9)

where:

 $\rm f_{lc}$ – probability density function of a random variable $\rm L_{c}$ of number of production cycles per shift,

 $\rm f_{td}$ – probability density function of a random variable $\rm T_{d}$ of available shift time,

 f_{tc} – probability density function of the random variable T_c of production cycle time.

Taking into account that random variables L_c and T_c take values from the set of positive real numbers, we obtain the following form of the formula

$$\begin{cases} f_{lc}(l_c) = \int_0^\infty f_{td}(l_c t_c) f_{tc}(t_c) t_c dt_c & for \ l_c > 0 \\ f_{lc}(l_c) = 0 & for \ other \ instances \ l_c \end{cases}$$
(10)

By substituting the calculated form of the function into equation (6), we will obtain the following form:

$$f_{qz}(q_z) = \frac{1}{w_c} \int_0^\infty f_{td} \left(\frac{q_z}{w_c} t_c\right) f_{tc}(t_c) t_c \, dt_c \tag{11}$$

The probability density function $f_{qz}(q_z)$ shown by the formula above identifies the probability distribution of extraction per shift. The probability density function for daily extraction is derived in a similar manner, as presented in (Snopkowski 1998).

In order to identify the probability density function of $f_{qz}(q_z)$ a random variable Q_z using the stochastic simulation method, the block diagram shown in Figure 2 must be implemented.

The generation of a realization of random variables according to certain functions takes place within the procedures (subroutines, functions), which are part of the computer program, implementing the process of stochastic simulation. A full description of the method enabling the identification of the functions listed in the scheme can be found in (Snopkowski 2007).

The probability density function obtained as a result of the considerations carried out in this chapter $f_{qz}(q_z)$ can be an additional instrument for planning the production activities of an enterprise.

The formulas derived also allow for the calculation of the probability of execution or the risk of non-execution of a particular mining plan (also calculated as the probability of such event).

4.2 Output stream intensity

Determination of the rate of the output stream intensity as a function of probability for a production cycle realized in longwall faces of hard coal mines is another example of using stochastic simulation in the analysis of a production process.

The output flow rate φ_{2k} is determined by the following dependence:

$$\varphi_{2k} = W_c / T_c \tag{12}$$

where:

T_c – production cycle time [min],

 W_c – production cycle output [Mg] is determined by the formula:

$$W_{c} = H \cdot z \cdot L \cdot \gamma \cdot \rho \tag{13}$$

in which the following parameters are:

H – wall height [m],

z – shearer outreach [m],

L – wall length [m],

 γ – coal volumetric weight [Mg/m³], ρ – take-up utilization factor [-].

After appropriate substitutions and transformations, the formula for determining the rate of excavation takes the following form:

$$\varphi_{2k} = \frac{H \cdot z \cdot L \cdot \gamma \cdot \rho}{\frac{1}{V_{cz}} (x_p - d_k) + \frac{1}{V_r} \cdot (L - x_p) + (\frac{1}{V_z} + \frac{1}{V_r}) \cdot (x_2 + d_k + p + s) + t_2 + t_5}$$
(14)

where:

V_{cz} - shearer maneuvering speed (shearer speed when clearing the shearer route) [m/min],

V_ - shearer working speed [m/min],

V_z - shearer working speed when cutting [m/min],

x_p - distance from the shearer stop position to the junction between the longwall and the gate road [m],

x, - distance of the advancing conveyor from support [m],

p - minimum distance of the advancing conveyor from the shearer [m],

 d_{μ} – shearer length [m],

t₂, t₅ - travel times for the crossover (drive) [min].

The calculation scheme to be carried out to determine the intensity of the output stream as a function of probability consists of the following steps:

Step I: Stochastic simulation of the index φ_{2k} for the assumed random variables, which is performed according to the scheme shown in Figure 3.

Step II: Determination of the empirical probability distribution of the index ϕ_{2k} , which is graphically shown in Figure 4.

Step III: Determination of the empirical distribution of the index φ_{2k} (Figure 5).

Determination of the empirical probability distribution of the output flow rate $\phi_{_{2k}}$ (stage II of the calculation) and the empirical distribution of the rate φ_{2k} (stage III of the calculation), makes it possible to evaluate the effectiveness of the production cycle (in essence, the evaluation of the rate of the stream of excavated material) as a function of probability.

Summary

Stochastic simulation is a research method offering many advantages. One of the most important ones is the ability to "observe" the studied process, using its computer model for this purpose. Running the model (simulation) multiple times makes it possible to obtain characteristics that are achievable by observing the real process over a long period of time, which in many cases is not possible. Stochastic simulation provides an answer to the question "what happens if...". What happens to the transportation system if we introduce one-way traffic in parts of it, where traffic jams will occur, what will be the average travel time, etc. What happens to a manufacturing system if we introduce machines with different reliability characteristics, to what extent will this affect its performance as a system.

This paper presents the use of simulation to identify the probability distributions of the extraction and the output flow rate obtained in the production process as an example of a stochastic simulation of the production process.

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