Dear readers and authors,

It is a great honour for me to present to your attention the new journal launched by the University of Mining and Geology "St. Ivan Rilski", Sofia, Bulgaria. The "Sustainable Extraction and Processing of Raw Materials" Journal (SEPRM) is envisaged as a specialised scientific publication aimed at presenting original and innovative research papers as well as concise reviews on the environmentally friendly and viable provision of resources from primary and secondary sources in order to contribute to the sustainable development agenda. It publishes also selected papers from the Annual International Scientific Conference of the University of Mining and Geology "St. Ivan Rilski", Sofia, Bulgaria. The official language of this double-blind peer reviewed journal is English. The following fields are covered:

- Geological and geophysical studies related to the assessment of mineral resources and their environmentally friendly extraction;
- Sustainable mining (underground and open pit, geo-technology - chemical, physicochemical, biochemical, and microbiological methods, urban mining, conservation, liquidation and reclamation of mining sites);
- Sustainable processing of primary and secondary raw materials - physical methods (communion, milling and dewatering), physicochemical separation methods (flotation, bio-, hydro-, and electro-metallurgy), mineralogical aspects and analytical techniques to follow the mentioned processes;
- Environmental issues, related to mining and raw materials processing, particularly those related to sustainable development;
- Modelling, control, economics and management of extraction and processing of raw materials.

The journal adheres to the standards of publication ethics recommended by the Committee on Publication Ethics (COPE) Core Practices.

I would like to thank all the prominent scientists who agreed to be members of the SEPRM Editorial board.
I would like also to express my deep gratitude to all reviewers and editorial staff for their time and hard work that have made this journal available.

Editor-in-Chief: Prof. Dr. Marinela Panayotova
CONTENTS

Anastasova, Y. Internet of Things in the mining industry - security technologies in their application 7

Asenovski, S., D. Kaikov. Open-pit time scale optimisation in a truck scheduling problem 11

Bimpilas, G.-M., G.N. Anastassakis. Magnesite beneficiation methods: a review 14


Doneva B., M. Delipetrev, G. Dimov. Seismic explorations for defining the damage to the earth dam Pishica in the Republic of North Macedonia 27

Georgiev, P., M.-F. Ivanova, M. Nicolova, I. Spasova, S. Groudev. Review of the iron recovery processes from laden leach liquors in hydrometallurgy 31

Gorbounov, Y., P. Peychinov. Laboratory model of a magnetic levitation system 37

Kaykov, D., I. Koprev. Rationalising the location and design of the waste dump in the case of open-pit mining 42

Kostadinova, N. Jet fans efficiency in tunnel emergency situations 47

Luganov, V.A., T.A. Chepushtanova, G.D. Guseynova, Y.S. Merkibayev, K.K. Mamygbaeva, B. Mishra. Processing of pyrite concentrates with the extraction of non-ferrous metals: nickel and cobalt technology elaboration 53

Minin, I., P. Nedyalkov, S. Savov, T. Hristova. Study of the relative energy consumption of a drum mill type SAG 8.5 x 5.3 59

Mollova, Z., V. Penev. Control of blast-induced seismic action generated by technological blastings 64

Moteva I., P. Georgiev. Effects of the iron oxidation and precipitation processes on the arsenate sorption and coprecipitation 68

Nikolova, K., S. Bratkova, A. Angelov, P. Genova, R. Ivanov, A. Stefanova. Treatment of sulphates-rich solutions through ettringite precipitation with industrial reagents 74

Petrova, V. Circular economy practices in the Bulgarian raw material industry 79

Stoycheva, N., P. Shishkov. Non-detonating charges in polymer housings for smooth splitting of rock blocks during primary extraction and secondary cutting 85

Toshev, S., A. Loukanov. Detection and monitoring of manganese in drinking water and groundwater through photo-oxidation sensory reaction with ultra-small carbon nanodots 90
INTERNET OF THINGS IN THE MINING INDUSTRY - SECURITY TECHNOLOGIES IN THEIR APPLICATION

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ABSTRACT. The Internet of Things are essentially huge networks of connected devices that collect and share data (information) both for specific processes and their application environment. The use of the Internet of Things (IoT) is changing every industry because it allows device-to-device communication and automates the maintenance, communication, and interaction between processes and their management. IoT gives businesses real-time information on how their companies’ systems work, significantly reducing labour costs. For this reason, more and more mining companies are taking advantage of the opportunities provided by IoT, creating their own networks of devices and communication environment. At the same time, IoT has become one of the most critical technologies of our century, due to the fact that cloud technologies and Wi-Fi networks, which are the basis of IoT, have become an attractive place for cyberattacks. The data collected by IoT sensors contain a huge amount of personal and company information, hence, it is especially important that they are securely stored and maximally protected. This article discusses some critically important technologies to ensure the security of IoT implementation and use in the mining industry.

Keywords: Internet of Things, mining industry, implementation, security technologies

Introduction

The Internet of Things (IoT) are gigantic networks of connected physical devices that collect, transmit, and share data about the environment in which they are embedded through sensors built into them (Arora, 2020). To make sharing possible, IoT provides a common platform and a common language for devices to communicate with each other. IoT is critical to any industry because digital systems record, monitor, and correct any interactions between the connected devices, providing real-time information about the company’s work. The mass penetration of IoT in every field and its continuous development has made it a preferred but also critical technology, because it is very important that the data collected and transmitted by various sensors are sent securely to the IoT platform (Hassija et al., 2019; Arora, 2020). The security and accuracy of the information transmitted are of particular importance in the mining industry, where minimal inaccuracy in the data can lead to major adverse consequences.

Security threats in IoT applications

In addition to the standard information security problems, the IoT applications used in the industry also face specific challenges such as problems with confidentiality, authentication, encryption, management, storage of information, etc. due to the peculiarities of the IoT environment.

As is known, in every IoT environment there are four particularly important layers (Fig. 1), which are used in every IoT application (Zhou et al., 2018; Arora, 2020).

The first layer called a sensory or recognition layer is the basic level. It involves the use of different types of physical equipment – sensors and devices – that collect all kinds of information, i.e. accept the data and can perform different functions. There are different types of sensors for the perception of data types, for example for camera, smoke detection, temperature maintenance, humidity, etc. In addition, sensors can be mechanical, electrical, electronic, chemical, ultrasonic, etc., but they all register changes in the real physical environment.

The most critical threats for this layer are the sensors themselves, as there is always the possibility of a malfunction that results in the submission of incorrect data that may cause incorrect actions.

The second layer, called network, uses a communication network to transmit the collected data. Its main function is the transmission of information obtained from the sensor layer for subsequent processing and analysis.

Since it uses different types of channels for the transmission of information, which do not always use encryption to a sufficiently reliable degree, it is always possible for the information transmitted to be intercepted and replaced with an unreliable one.
Since IoT uses different data transit technologies (depending on the type of data transmitted by different types of sensors), this makes the data in transit much more vulnerable to cyber-attacks such as DDoS, routing redirection, intercepting the real information and replacing it with fabricated data, etc.

The third layer in IoT, called middleware, acts as a bridge between the network and the application layer, providing powerful computational capabilities and possibilities for the permanent storage of the transmitted data. Many IoT apps use this layer to provide reliability and security of the apps themselves. It usually includes data repository, various web and cloud services.

This layer is also vulnerable to attacks on both web services and databases where the catalogued information is stored. It is susceptible to man-in-the-middle, SQL injection, flooding, etc., attacks.

The fourth, application layer directly provides functions and services to end users. Various end-to-end IoT applications such as smart grids, smart transportation, smart mines, smart cities, etc. are based in the fourth layer. In this layer, depending on the application used, there are specific security issues that are not present in the other layers. The application layer is susceptible to attacks such as data theft, access control, denial of service and privacy issues.

Hence, each of the four layers in the IoT environment has specific security issues. It is important to note that due to the heterogeneity of the information supplied by the sensors and the specific application, different gateways are located between the layers, which connect them and help the movement of data between them. These gateways also have specific data security issues.

For the most part, IoT applications use cloud services to store and retrieve data and information, and the risks caused by the cloud must be taken into account (Zhou W. et al., 2018). Cloud is a public platform used by many users and there may be malicious users who could be a threat to IoT-related data. This is an additional security challenge.

Judging from the above, ensuring the security of the IoT environment is much more challenging than providing standard information technology (IT).

**Application of IoT in the mining industry and security technologies used**

In the last 10 years, IoT applications have entered the industry on a large scale, being the main engine for the development of the fourth industrial revolution - Industry 4.0 (Bakhshi et al., 2018; Hassija et al., 2019). Mining companies that make huge investments in their production are also part of this development.

One of the key factors for the wide entry of IoT applications in the mining industry is related to the harsh and unfavourable working conditions. It is also important that the response time in case of emergencies in this industry is too short and thus, the workers' reaction is not always feasible.

One of the first areas in which the implementation of IoT applications in general and in the mining industry began is the so-called smart transport. All modern cars have a central computer that monitors the operation of the engine and various functions of the car through different sensors.

In the transport systems in mining companies, where the working conditions and the machines themselves are heavier than the standard ones, many different IoT applications are used.

In companies that develop open cast deposits and where transport systems are especially important, different types of sensors are built into the dump trucks that have big capacity – from 80 to 300 tons, which monitor not only the operation of the engine but other particularly important indicators as well. Due to the peculiarities of the terrain and the weight of the machines, there are IoT applications that monitor the angle of inclination of the terrain, the pressure in the tyres, the fuel consumption on climb or descent, the distribution of the load, etc.

When developing underground deposits, IoT applications are used to monitor the volume of emitted gases, the temperature of the main nodes and the condition of the working units, the depth of drilling and other important parameters for each particular mining machine.

In the last decade, due to the harsh working conditions, remote-controlled machines have started to be used in the mining industry, with various IoT applications or trained operators to work with them – i.e. the subjectivity of the human factor is largely avoided.

In both types of deposits, the data that comes from each particular IoT application, device and smart machine is transmitted to a cloud structure where they are processed and permanently stored. On the basis of the information received, a comprehensive logistics system for the management of the equipment is created, which optimises the transport functions. Thus, the stay of the machines, the unnecessary load or collisions in the work are avoided, since the transport is only part of the overall mining process in the mining industry.

Another very important strand in the mining industry and the underground construction is the use of IoT’s applications for control of the air conditioning systems and air circulation. The supply of a clean jet of air is critical in the underground development of deposits, and all their work depends on it.

In addition to powerful fans, modern ventilation systems include a large amount of sensors that analyse in real time the quality and quantity of the airflow and, depending on the parameters, can adjust it. At the same time, they are associated with the so-called ventilation barriers that are automatically activated by the relevant sensors and maintain the air quality in a given horizon, face or a specific workplace.

In the mining and underground construction industries, the sensors that control the quality and quantity of the airflow are always duplicated to ensure a high level of security. Moreover, the location of the sensors is of particular importance so that the data they collect can give an accurate and real picture of the air conditioning process.

Another area in which IoT applications in the mining industry are used is the processing of extracted minerals, where depending on its type different types of sensors monitor the process and automatically manage the addition of the necessary reagents.

The diversity of IoT applications used in the mining industry, the availability of different types of sensors and the availability of different types of communication protocols, as well as the use of Wi-Fi networks significantly hinder the security. In addition, many of the systems used in the mining industry use GPS to monitor and track transport systems or specific processes, which further complicates the problem.

Each IoT application used in the mining industry consists of a large number of different sensors and connected devices and a variety of protocols and technologies. The cost-effectiveness of IoT, the delays in transmission of information, the reliability
and security of the IoT environment must be provided already at the design stage of the IoT environment for a specific application. It is also important to anticipate its development and scale (Blyler, 2017).

The security technologies that apply to IoT applications in the mining industry can be summarised in several large groups:

**Security of sensors providing data for the IoT application**

All sensors and devices that transmit data and perform different functions regardless of the specific IoT application should be certified and compliant with the overall architecture. When performing functions that are critical from the point of view of the mining industry, it is obligatory for each sensor to be duplicated in order to ensure the continuity of the supplied data flow.

Periodic inspection and calibration of the sensors is necessary, as it is possible for them to fail and start transmitting incorrect data. In case of any suspicion of deviation from the usual values, it is necessary to check and validate the information supplied by the sensors. In a distributed architecture, as is usually the case in the mining industry, it is mandatory to correctly select the location of the individual sensors in order to avoid distortion of the information supplied.

**IoT Authentication**

A mandatory security condition in each IoT application is to include different mechanisms for authentication of devices and entities. Depending on the required level of security, the technologies used can be varied. Generated static passwords can be used for device authentication, two-factor authentication, digital certificates, and biometric data for objects and entities.

It is also necessary to use authentication in data transmission protocols, which can be implemented through digital authentication certificates, additionally linked to cryptographic protocols.

It is important to note that most of the authentication technologies used in IoT applications do not involve human intervention - i.e. the checks are carried out through M2M communication, which guarantees additional security.

**IoT Network Security**

The network security requirements for IoT differ from those for standard networks, as the variety of communication protocols, standards, and device capabilities create significant problems and increase complexity.

It is mandatory to use firewalls and systems to isolate the network of a particular mining company from external interference, e.g. communication with external systems must go through anti-virus scanning and check for other malicious code or software.

To ensure network security, it is imperative to install systems to detect and prevent intrusion into the company’s network.

**IoT Security of the Application Programming Interface (API)**

The technology which ensures the security of the API in IoT applications protects the integrity of the data when transferring them between end devices (sensors, etc.). It certifies the end devices and accordingly allows or blocks the transfer of data, allowing communication only between authorised devices, users and IoT applications.

It is also possible to have a functionality that monitors the detection of potential threats and attacks against the API.

**Encryption Use**

Encryption techniques are used in a specific IoT application and in the whole system at different layers and protocols. Depending on the parameters of the individual devices (sometimes insufficient sensor memory), there are different levels of encryption, decryption and re-encryption throughout the system.

End-to-end encryption is the most effective solution to prevent various attacks, but the hardware capabilities of the devices, which can create problems with their speed and performance, must be taken into consideration. At the same time, it is important to constantly monitor the proper management of the keys.

IoT applications use encryption, RSA, SHA256-based or hash-chain technologies that can protect data from theft or tampering.

Starting from the design stage of an IoT application, the terminal devices must be selected in such a way so as to ensure the transmission of sensitive data in a sufficiently secure and encrypted manner.

**Cloud Security**

For the most part, IoT applications use cloud services to store, process, and retrieve data. This suggests that when using a particular IoT application, the risks that may come from the cloud must also be anticipated.

If a public Cloud platform is used, it is possible to have malicious users in the cloud, who can threaten the confidential information related to a particular IoT application in the mining industry. In this case, data encryption by authorised devices and users is mandatory.

When using a large number of IoT applications and a corresponding increase in the number of sensors and functionalities, it is recommended that mining companies create their own cloud, which guarantees them a much higher degree of protection and security of the transmitted data.

**IoT Security Analytics**

The ultimate goal of all IoT applications in the mining industry is to create an autonomous system that requires minimal human intervention. For this reason, techniques or algorithms based on artificial intelligence (AI) are used to analyse the processing of information and communication on the IoT environment. These solutions add machine learning, artificial intelligence and big data processing to the IoT environment, providing predictive modelling and anomaly detection.

Security analysis of IoT applications and environments is also used to detect IoT-specific threats and attacks that are not identified by traditional security solutions.

**Conclusion**

The use of IoT applications allows access to information from anywhere at any time to any device via M2M communication. The transfer through an IoT environment allows data to communicate and share between electronic devices and translate them in the way we want.

IoT makes systems in the mining industry efficient by saving costs and energy, as physical objects are controlled and digitally...
connected to a wireless infrastructure, allowing maximum automation and control.

At the same time, the large number and variety of IoT devices and communication protocols pose challenges to the collection, processing and management of data from all these devices in terms of security and protection. The use of wireless connectivity and cloud technologies in the IoT environment requires additional security measures.

The presented technologies for ensuring security in IoT applications, applicable in the mining industry, are a combination of traditional and new methods and technologies, which guarantee cybersecurity.

At the same time, the use of the security technologies should not hinder the operation of the IoT application, which may make it unacceptable for use due to delays and additional checks.

References


OPEN-PIT TIME SCALE OPTIMISATION IN A TRUCK SCHEDULING PROBLEM

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ABSTRACT. In the present economic situation, the open-pit mining processes require flexible solutions for achieving the set goals. The aim of the study is to consider a comprehensive mathematical model for a short and long term open-pit mine optimisation in a truck scheduling problem. The model can be applied in different situations with various number of units and trajectories depending on the landscape of the area in question. Significant amount of parameters modulating the discussed processes is analysed.

Keywords: time scale optimisation, truck scheduling

Introduction

The need to increase the quality and quantity of mineral raw materials requires the use and development of complex mathematical models that take into account a larger number of variables in the open pit mine system. The complexity of these mathematical models requires the availability of qualitative information for the variation of the basic parameters of the mineral raw materials or coal (annual productivity, product prices, ash content, humidity, etc.). Proper collection and storage of information can be a key point in choosing an optimisation method and analysing the results.

In the processes of excavation and digging of the mineral raw materials or technogenic waste different problems emerged, most of which are not included in the plan of the open pit operation (Grigorova and Koprev, 2017; Koprev and Kaykov, 2017). Such short time scale problems, for example, the decision of the engineer to mine or not every next block, need to be solved with the methods suitable for such situations. These methods are different from those which should be used in determining for example the shape and size of the open pit, ore recovery, extent of the deposit, etc.

Long and short-term planning in surface mining determine the optimisation of scheduling problem (Dagdelen, 1986; Osanloo et al. 2008; Amankwah, 2011). While the long-term schedule determines most of the based engineering decisions including equipment selection, maintenance planning, dispatching and so on, the short-term production scheduling is focused more or less on unpredictable difficulties or features in the mining process.

Several studies have examined aspects of the truck scheduling problem (Frimpong et al., 2002; Yang et al., 2006; Chang et al., 2015). Here we study this problem in the long and short-term planning context. We seek to characterise the main difference in modelling when time variable exists.

If we consider the well-known “block model” of planning extractions in open pit mines (Espinoza et al., 2013) (Fig.1), a long-term scheduling (at least several months or years) determines the consistency of the extraction. In that sense, the first and the most important note related to the present studies is determining the time periods that distinguish what are “long” and “short” periods.

Because of the complexity of the truck scheduling problem, a number of software products based on the optimisation linear models have been developed. Most of them are quite applicable when we consider long-term scheduling, but generally results are far from optimal.

Motivation

The development of usable mathematical algorithm of the time scale optimisation in the truck scheduling problem is motivated by constantly growing goals of economic profit. The efficient solving of this problem leads to reduction of the transportation cost, and increase in the mine productivity (Alarie and Gamache, 2002).

Trucks are essential element in open pit mine equipment and generally they are used for ore and waste transportation between loading points (L) and dumping depots (D) (Fig.2 (a)). One important note here is that the location of D is relatively constant in time, while the location of L varies.

Most of the research related to the problem is focused on the production planning or pit design (Newman et al., 2010), pit limit design and block sequence problem (Wright, 1989; Klingman and Phillips, 1988). Knowing that the long-term schedule can be considered as a vital part of the mine project, we also assume that it is crucial for short-term decisions. Some authors divide the truck scheduling problem into different stages. For example, White and Olson (1992) analyse three phases – shortest path problem, which is the shortest path between all locations L and D; the second phase is calculated with linear optimisation of the material stream between L and D; and the third – optimisation of the paths.

In this paper we have tried to implement different views of the problem using an extended mathematical algorithm.

Description of the problem

Usually in each open pit mine, there are several loading points L and dumping depots D. In most cases the number of L is bigger than D (Fig.2 (a)). We assumed that each loading point L is supplied with only one electric shovel. In other words, one loading point corresponds to one electric shovel. We assume also that the set of accessible trucks T are loaded by electric shovels in each loading point and the trucks unload themselves on the dumping points.
The following different times periods for the whole process must be included:

- \( t_l \) - loading times per truck by electric shovel \( i \);
- \( t_u \) - unloading times per truck in depot \( j \);
- \( t_{0} \) - time for a loaded truck to move from the electric shovel \( i \) to the dumping depot \( j \);
- \( t_{l} \) - time for an empty truck to move from the depot \( j \) to the electric shovel \( i \);
- \( t_{u} \) - time for a truck to move from the waiting area to the electric shovel \( i \);
- \( t_{0d} \) - waiting time for a truck on a depot waiting area.

The choosing of time periods in which we will analyse the truck scheduling problem actually is the basis of our study. That is why we introduce the time periods’ variable as follows:

\[ H \rightarrow \text{the time horizon considering the problem;} \]
\[ A \rightarrow \text{related variable with } H \text{ is:} \]
\[ m \rightarrow \text{maximum number of trucks loading by electric shovel } i \text{ during the horizon period } H, \]

**Integer modelling**

For the purpose of the mathematical modelling a few decision variables are introduced:

\[ x_{i0} = \begin{cases} 
1, & \text{if truck } T_k \text{ has } t_0 = 0; \\
0, & \text{otherwise.}
\end{cases} \quad (1) \]

\[ z_{ij} = \begin{cases} 
1, & \text{if truck } T_k \text{ is loaded;} \\
0, & \text{otherwise.}
\end{cases} \quad (2) \]

\[ u_{ij} = \begin{cases} 
1, & \text{if truck } T_k \text{ has } t_{0d} = 0; \\
0, & \text{otherwise.}
\end{cases} \quad (3) \]

In the context of the optimisation the best solution of given variables from equation (1) – (3) is when we have \( x, z \) and \( u \) equal to 1. In other words, trucks do not stand in waiting area.

The sum of all introduced times gives the expected real time of one truck \( T_k \) scheduling:

\[ t_{\text{exp}}^k = t_l + t_u + t_{ij} + t_{0d} \quad (4) \]

Other decision variable can be introduced concerning truck scheduling in terms of routes:

\[ y_{ij} = \begin{cases} 
1, & \text{if } T_k \text{ is loaded at } i \text{ and dumped at } j; \\
0, & \text{otherwise.}
\end{cases} \quad (5) \]

Now let’s consider the most important times for the purpose of our investigation – waiting times \( t_o \) and \( t_{0d} \). As far as these times concern one truck \( T_k \), we can introduce the expected real times for waiting in the electric shovel waiting area and the dumping depot waiting area, respectively:

\[ t_{\text{exp}}^0 = \sum_{k=1}^{N} t_{0}^{k} = t_{0}^{1} + \ldots + t_{0}^{k-1} + t_{0}^{k} + t_{0}^{k+1} + \ldots + t_{0}^{N} \quad (6) \]

\[ t_{\text{exp}}^{0d} = \sum_{k=1}^{N} t_{0d}^{k} = t_{0d}^{1} + \ldots + t_{0d}^{k-1} + t_{0d}^{k} + t_{0d}^{k+1} + \ldots + t_{0d}^{N} \quad (7) \]
where $N$ is the total number of trucks.

If two trucks are in the same time at the waiting area, the waiting time of the second one is the sum of the waiting time of the first truck, the time of the truck to move from the waiting area to the loading point and the time for loading of the first truck:

$$t_0^k = t_0^{k-1} + t_{0i}^{k-1} + t_{i}^{k-1}$$  \(8\)

We assume that the time for a truck to move from the waiting area to the electric shovel is the same for all trucks and all loading times are equal:

$$t_{0i}^{k-1} = t_{0i}^k = t_{0i}^{k+1}$$  \(9\)

$$t_{i}^{k-1} = t_i^k = t_i^{k+1}$$  \(10\)

Using (8), (9) and (10), in (6) we received:

$$t^0_{exp} = 2(N-1)(t_{0i}^1 + t_i^1)$$  \(11\)

Similarly, in (7) we have:

$$t^{0d}_{exp} = 2(N-1)t^1_j$$  \(12\)

The truck scheduling problem can be formulated as:

$$2(N-1)\sum_i \sum_j (x_{ij} t_{0i}^1 + (1-z_{ij}) t_i^1 + u_{ij} t_j^1) \rightarrow \text{min} .$$  \(13\)

The function (13) of the model minimises the sum of the expected real time of the truck waiting on the electric shovel and depot areas.

Several constrains can be added:

$$\sum_j x_{ki} = 1 ,$$  \(14\)

which correspond to the assumption that only one truck can be loaded by one electric shovel at a time.

Similarly, for dumping depots we have:

$$\sum_i u_{ij} = 1 ,$$  \(15\)

$$\sum_i z_{ki} = 1 \text{ and } \sum_i \sum_j y_{ij} = z_{ki}$$  \(16\)

are constraints corresponding to the assumption that there is at least one truck at a time that is loaded.

A few other constrains about providing each truck enough time for loading, unloading and traveling time when the truck is loaded and empty can be summarized:

$$t_{exp}^k - t_{exp}^{k-1} \geq t_i$$  \(17\)

$$t_{exp}^k - t_{exp}^{k-1} \geq t_j$$  \(18\)

$$t_{exp}^k - t_{exp}^{k-1} \geq t_0$$  \(19\)

**Conclusion**

In the present paper, open pit time scale optimisation in a truck scheduling problem have been examined. The formulation of the model is based on the waiting truck time in the electric shovel and dumping depots areas. Several constrains are assumed.

**References**


MAGNESITE BENEFICIATION METHODS: A REVIEW

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ABSTRACT. Magnesite is one of the most important mineral commodities mostly because of its technological and industrial applications. The most important commercial sources for its recovery are the corresponding ores. The deposits are characterised by the differences in reference to magnesite mineral crystallinity and gangue composition. For these reasons, the separation efficiency of magnesite from gangue varies from relatively easy to impossible. Another problem is the stocked waste, often of relatively high-grade in magnesite, derived from industrial processing, which may be viewed as future potential deposits. This paper contributes a detailed review on the methods applied to separate magnesite from gangue both on industrial and bench scale; potential processing methods for fine particle size are also reviewed.

Keywords: separation methods of magnesite, magnesite processing, magnesite flotation, serpentine

Introduction

Magnesium is the eighth most abundant element of the earth crust and the third one in the sea-water with average concentration of 20,900 ppm and 1,350 mg/l correspondingly (Mason and Moore, 1982; Theodorikas, 2014). Magnesium is encountered in many minerals, both siliceous and non-siliceous. In the non-siliceous minerals the following are included: the carbonate ones magnesite (MgCO₃) and dolomite (CaCO₃·MgCO₃), the hydroxylated form brucite [Mg(OH)₂], and the minerals of evaporate group carnallite (KCl·MgCl₂·6H₂O), bischofite (MgCl·6H₂O), kieserite (MgSO₄·H₂O) and brunerite, which is a solid solution of magnesium carbonate and iron carbonate, with its FeCO₃ content ranging between 5 and 30%. Among the siliceous minerals the most important are olivine [(MgFe)₂SiO₄], talc [H₂Mg₃(SiO₄)₂] and serpentine [H₂Mg₃Si₄O₁₀].

From the magnesite rock mined, only a small part is used to produce magnesium metal while the great majority is directed to industrial uses, with magnesite being the most important mineral from the commercial point of view. The most important magnesite products are raw magnesite, caustic calcined magnesia, dead-burnt magnesia and refractory mass. Magnesite is white coloured, chemically inert, soft enough and good absorbent. Because of these properties, it is used as primary raw material in a wide spectrum of industrial applications, such as: ceramics and refractories, steel production, magnesium metal and alloys production, cement industry, fertilizers and cattle feed, environmental depollution, pharmaceuticals, etc.

Magnesite ore deposits

Magnesite is encountered in two forms with different structure: microcrystalline and crystalline. Although crystalline magnesite deposits represent more than 90% of the global deposits, the microcrystalline ones are commercially more preferable due to their higher quality and advantages (Pohl, 1990).

The microcrystalline form is also referred to as cryptocrystalline or amorphous (Nasedkin et al., 2001), but these terms do not correspond to reality because magnesite grains do present crystallinity but their size is very small (between 1 and 5 μm). The small magnesite grains are aggregated to form a compact rock with conchoidal fracture, which is characterised by high MgCO₃ content (sometimes reaching up to 87 - 90% MgCO₃); in some cases, the aggregates have porous structure, with pores’ size between 20 and 80 μm, which provides them with higher specific surface and activity compared to the crystalline.

The genesis of microcrystalline magnesite is due to the alteration of ultramafic rocks of ophiolitic complexes (e.g. serpentine, peridotite); this form is encountered as variable size veins within the mass of the host rock. Due to its genesis, the gangue minerals are mostly composed of serpentine, various SiO₂ forms (quartz, opal, chalcedony), calcite and dolomite; minor gangue minerals are iron and aluminium oxides, talc [Mg₃Si₄O₆(OH)₂], chlorite ([Al, Fe³⁺, Fe²⁺, Li, Mg, Mn, Ni]₃[Al, Fe³⁺, Si]₂[Si₄O₁₃](OH)₂], etc. Microcrystalline magnesite may also be of sedimentary origin as layers intercalated with calcite, dolomite, or clayey layers (Davis, 1957).

On the contrary, crystalline magnesite is composed of sparry grains, with their size usually ranging between 0.5 and 20 mm, and, in some cases, even so large as 5 to 6 cm (Nasedkin et al., 2001). The major gangue minerals are dolomite and calcite; the minor ones are serpentine, talc, chlorite, quartz, hematite, diopside, diopside (CaMgSi₂O₆), tremolite (CaMg₃Si₂O₇(OH)₄), etc.

Due to the huge demand for magnesite products and high quality refractory materials, it is a necessity to remove the impurities from the host rock by mineral processing methods. The increased levels of miscellaneous impurities (e.g., CaO, SiO₂, Fe₂O₃, Al₂O₃) have a detrimental impact on the efficiency of the process and the properties of the refractories. The depletion of the high-grade and high-purity magnesite deposits along with the continuously increasing demand for magnesite products lead to the urgent need to focus on the processing of lower grade deposits.

The chemical composition of raw magnesite, after mining or beneficiation, determines its suitability for the various uses and the quality of products after calcination. It must be pointed out that there are no certain limits for the determination of the product quality, because quality is not determined solely by MgO content but from the content of the impurities as well; the presence of impurities (such as CaO, SiO₂, Fe₂O₃ and Al₂O₃) in magnesite products usually render difficult the processing and adversely affect refractoriness. From quality point of view, the commercial specifications of magnesite are not standard. Magnesite for caustic calcined magnesia, which is the main feedstock for refractories, is considered commercial for MgO content higher than 40% (corresponding to 84.0% MgCO₃). Internationally, the specifications of commercial magnesite for
refractories range between: MgO 40-47% (or MgCO₃ 84.0-99.0), CaO 0-3.5%, SiO₂ 0-7%, Fe₂O₃ + Al₂O₃ 0-3% (Minerals and Refractories, 2020).

Due to the diversity of gangue minerals, their similar properties with magnesite and the high commercial importance of magnesite, extensive scientific work has been carried out on magnesite beneficiation. The target of the current paper is to critically overview the processing methods related to magnesite separation both at industrial and laboratory scale.

**Magnesite Processing Methods**

**A. Industrial scale**

At industrial level, the separation method to be applied depends on gangue minerals, product specifications and processing cost. The industrial separation schemes for magnesite usually include the following methods:

- **Optical (or visual) sorting.** This is a common practice to separate magnesite (white) from coloured gangue minerals (e.g. serpentine). This principle has been applied in the past as hand-sorting for coarse particles or, currently, as digital sorting with laser beam or camera for particle size 4-10 mm (GRECIAN MAGNESITE 2020).

- **Magnetic separation,** which has been used to remove magnetic gangue. Dry high-intensity magnetic separators with superconducting magnets have also been used (GRECIAN MAGNESITE 2020).

- **Gravity heavy media separation** has been used to remove silicate minerals and dolomite (light product) from magnesite (Rau, 1985; GRECIAN MAGNESITE, 2020). Due to the slight difference between their specific gravity, this procedure is not always efficient; hence, further processing by magnetic separation or visual sorting is often required to improve the results (Frangiskos et al., 1981).

- **Flotation** has relatively limited industrial application to separate gangue from magnesite (Rau, 1985). In general, magnesite can be economically separated by flotation from silicate gangue minerals but not from carbonates. The flotation scheme to be used depends on the nature of the minerals involved. In case the ore has increased percentage in silicates, reverse flotation can be used in the presence of cationic collectors’ mixture. By this process, high quality product is produced, suitable for dead burned magnesite production. This practice has been industrially applied, developed and patented at Mantoudi (Euboea, Greece) magnesite mineral processing plant (Gambopoulos and Nestoridis, 1976).

**B. Laboratory scale**

The need for high purity MgO has increased in the last few years; as a result it is vital to apply more efficient methods to separate magnesite from gangue minerals targeting products of higher purity. The methods that meet these requirements are gravity methods for coarse particles (>1 mm) and flotation for fine particles, especially if high-grade product is required.

Due to the wide spectrum of applications and the required high quality standards of magnesite products, extensive research has been carried out at lab-scale to solve practical problems that prevent the complete separation of magnesite from gangue minerals, especially carbonates. To meet the target, various physical and physicochemical methods or combination of methods have been tested, with most of them being devoted to separation by flotation.

**Physical Separation Methods**

Back in 1970s, a separation method that includes calcination of magnesite ore at 600 - 800°C and subsequent gravity separation of the calcined product on a Berry air-separator was developed in the laboratories of the former Skalistiri group (Euboea, Greece) and successfully applied. (Frangiskos and Kontopoulos, 1976). The separation scheme provides very good results in the case of serpentine and other silicate gangue minerals, due to the significant enhancement of specific gravity difference between magnesite ore and gangue minerals after calcination.

Similar scheme was applied in another magnesite processing plant in Greece, located at Vavdos, Chalkidiki; in this case, it must be pointed out that, after calcination, gravity heavy media separation was applied instead of air-separation (Frangiskos, 1995). In addition to the industrial schemes, lab-scale tests including calcination and multi gravity separation (MGS) achieved encouraging results in terms of MgO content but with relatively low recovery (Gence, 2001). Through this process, a concentrate containing 78, 14 MgO, 1,51% CaO and 0,55% SiO₂ was obtained, but the recovery in MgO was only 57,21%, while the feed content was 44.87% MgO, 3,1% CaO and 0,5% SiO₂.

Suslikov et al. (1966) attempted to separate magnesite from dolomite by exclusively applying heavy media (gravity) separation. According to the results, the concentrate of magnesite was of high purity, with 82-84% weight recovery, while a high purity dolomite product was obtained as well.

Other researchers combined calcination with subsequent high intensity dry magnetic separator testing on magnesite ore of fine particle size and intimate association of magnesite grains with gangue constituents. The separation yielded encouraging results but further improvement is necessary for industrial application (Potapanenko et al., 1981). The same methodology was applied to middling product derived from magnesite processing. The results of the research showed that it is possible to produce a marketable product with 89.5% MgO content and low content in harmful constituents (Bentli et al., 2017). A similar procedure (calcination and magnetic separation) was tested on magnesite ore with high impurities content from Slovakia, which resulted in a product with 82,77% weight yield, 81,91% MgO content and 89,19% MgO recovery (Hrédžak et al., 2014).

Contrary to magnetic, Cao et al. (2016) applied electrostatic separation to raw magnesite ore of very fine particle size (<20 μm) without particular success with regard to the removal of gangue minerals (quartz, dolomite, calcite, chlorite and talc). On the other hand, researchers from the former Soviet Union applied photometric and radiometric separation to magnesite deposits with dolomite, calcite, chlorite and quartz as gangue minerals, with particle size 8-150 mm (Rogozina et al., 1989, 1990). The tests lead to particularly satisfactory results, as the concentrate produced was of high MgO content (90-92% MgO). Other researchers (Aksel’rod et al., 2016) applied X-ray separation that resulted in a product with SiO₂ and CaO content less than 1,1 and 2,1% respectively.

Due to the difficulty of separating magnesite from gangue minerals, especially carbonates, a significant portion of magnesite is lost to the tailings and middlings, which are deposited as piles for potential future exploitation. It should be noted, however, that the removal of calcareous impurities is much more difficult, even impossible, than that of silicate impurities. At present, large tonnage of such magnesite-containing material has been deposited onto piles as gangue,
because it can’t be processed at low cost; however, it is a potential magnesite source, when an economically viable processing scheme is invented. As a result, a considerable part of the research efforts has been devoted to the recovery of magnesite from middlings and tailings, regardless of the separation schemes applied.

In Greece, the research was focused on the exploitation of the material of particle size -40 mm that had been deposited onto piles as tailings from previous separation (Dimopoulos, 2012, Dimopoulos and Anastassakis, 2013). The methods examined were hand-sorting on belt, heavy-liquid separation and magnetic separation. Hand-sorting, which was applied to particle size -40+10 mm and -10+4,75 mm, provided concentrates with recovery and content in MgCO₃ both higher than 90%. Heavy-liquid separation, which was applied to particle size -10+4,75 mm, provided with concentrate of 95% MgCO₃ with 72% recovery. As regards magnetic separation, the size fractions used were -10+4,75 mm, -4,75+2,36 mm and -2,36 mm. The grade of the concentrates ranged between 80 and 87% MgCO₃ while the recovery was of the order 90%, except the fraction -2,36 mm, whose recovery was about 60%.

Physicochemical Separation Methods

Since magnesite paragenesis involves minerals with similar physical properties and gangue separation is not always easy, especially in fine particles, a great share of the research on lab-scale has been focused on flotation. As mentioned before, the major gangue minerals are silicates (mainly talc, serpentine, quartz) and carbonates (dolomite and calcite). The type of impurities and their proportion in the ore directly affect the flotation results. From the aforementioned gangue minerals, silicates, quartz and iron oxides present different physicochemical behaviour during flotation in comparison to that of magnesite and, therefore, their separation is relatively easy. On the contrary, dolomite and calcite have similar physicochemical properties and behaviour to magnesite; consequently, their separation by flotation is difficult even with the use of regulatory reagents.

The efforts to separate the aforementioned minerals by flotation have been undertaken upon the depletion of the high-grade magnesite deposits. Based on their experimental results, Doemer and Harris (1938) suggested that magnesite can be separated from silicate gangue minerals by flotation at neutral pH, in the presence of sodium alkyl sulphonate collector and caustic soda depressant.

In the United States, other researchers have tried to separate magnesite from gangue minerals that accompany it (dolomite, calcite, silicates) by applying one or two flotation stages with proper collectors and regulatory reagents on a case by case basis. These methods have been patented (Doemer and Harris, 1940; Fahrenwald, 1942; Hellmann, 1950; Jepsen, 1972). Lefforge (1945) also used flotation to separate magnesite from serpentine, chromite and anthophyllite (< 100 µm) with oleic acid collector.

In the case of silicate minerals as major gangue, they are easily separated by reverse flotation. This method has been applied on industrial scale and, as previously mentioned, has been patented by Greek researchers with international patent (Gambopoulos and Nestoridis, 1976). Laboratory tests have also shown that it is possible to separate magnesite with anionic collectors (Rau, 1985).

Reverse flotation is usually used when a high-grade magnesite concentrate is required; in this case, cationic collectors are used to remove silicate minerals. The most common collector used on a lab-scale is dodecylamine, while low cost amine mixtures are used on industrial scale. Also, several novel cationic collectors have been used to separate quartz from magnesite (Breznai et al., 2017; Liu et al., 2019), with satisfactory results on lab-scale but not tested in practice. On lab-scale, Karantzavelos (1984) has also applied two flotation stages to low-grade magnesite deposits with silicate gangue. The first stage includes flotation with primary amine collector to produce rough magnesite concentrate, which contains silicate minerals. Subsequently, the rough concentrate is subjected to a second flotation stage with quaternary amine collector aiming at floating of the harmful impurities. The results showed that it is possible to obtain a cleaner concentrate of high-grade in magnesite and low in impurities (0.99 - 0.20% SiO₂ and 2.84 - 0.46% CaO). By adjusting the parameters that control the flotation effect, it is possible to achieve CaO:SiO₂ ratio between 0.32 and 5.79, which are the acceptable limits to produce dead-burned magnesia.

Karanika (1992) dealt with the separation of cryptocrystalline magnesite deposit, with serpentine as major and hematite/calcite as minor gangue minerals, by flotation or combination of methods that include flotation. The target was to utilise the tailings (with particle size -2 mm) of the magnesite processing plant located at Paraskeviora Mantoudi (Euboea). The conclusions of the research are summarised to the following:

a) The direct flotation of magnesite with cationic collectors (Armac C and Armac T) and various modifiers (sodium silicate, phosphates) were not successful, because of the high content of the concentrate in impurities.

b) The combination of direct flotation (magnesite flotation) using anionic collectors (fatty acids) and reverse flotation using cationic collectors (amines), provided with concentrates of acceptable content in impurities.

c) The combination of pre-concentration with high-intensity dry magnetic separation and subsequent reverse flotation (serpentine flotation) using cationic collectors (amines) produced concentrates with acceptable content in SiO₂ and Fe₂O₃ but not in CaO. However, it should be pointed out that, in cases where flotation was applied, the reagents consumption was high.

Gence and Ozdag (1995) studied the surface properties of magnesite and serpentine in the presence of various collectors (oleic acid, sodium oleate and Armoflote 14) and sodium silicate, which was used as serpentine depressant during anionic flotation of magnesite. Tests on mineral mixture with 90% magnesite showed a slight improvement of the concentrate (1 to 2 points) compared to the original content, but with 70-80% magnesite recovery.

Also, Santana and Perez (2000) were involved in the production of high purity magnesite concentrate (SiO₂ content less than 0.20%) and magnesite recovery by weight greater than 84%. These researchers applied reverse flotation (silicates flotation) using amine collector and corn starch as magnesite depressant with satisfactory results. They achieved high purity magnesite concentrate, with quartz and other silicate content of 0.17%, and weight recovery of approximately 92%.

Similarly, Aslani et al. (2010) applied reverse cationic flotation to magnesite deposits in eastern Iran to remove silicates using sodium silicate as magnesite depressant. According to the results, it seems feasible to remove silicates
and produce magnesite concentrate suitable for use in the magnesium refractory brick industry.

Chinese researchers (Li and Liu, 2015) carried out experimental work on deposit, in the province of Liaoning, with high content in silicates and low in magnesite, applying reverse flotation for the silicates and direct flotation for the magnesite; the separation scheme included one stage of rough flotation and two cleaning stages to remove silicates. The second cleaner concentrate had the following content: 47.48% MgO, 0.21% SiO₂ and 0.76% CaO while magnesite recovery was 65.46%.

Other Chinese researchers (Wei et al., 2012) carried out tests on low-grade magnesite deposit with finely disseminated quartz as major gangue mineral. After very fine grinding (92.6% was <0.074 mm), they applied reverse flotation of quartz with lauric amine 350 g/t and, subsequently, direct flotation of magnesite with sodium oleate (1500 g/t) and sodium silicate (3500 g/t) as depressant of the remaining silicates. This treatment resulted in concentrate with 46.85% MgO and 1.21% SiO₂.

Chen and Dai (2016) tested reverse flotation on magnesite deposit with relatively low content in gangue minerals (mainly talc and dolomite). By using amine collector and hexametaphosphate or sodium silicate as magnesite depressants, they achieved slight improvement of the initial MgO content.

Reverse flotation has been used to remove silicates from magnesite with dodecylamine collector, after prior treatment with bacteria (Teng et al., 2018). For comparison, tests were also performed without pre-treatment with bacteria. The results showed that without pre-treatment with bacteria the concentrate content was 4.61% SiO₂, while after treatment the content in SiO₂ was reduced to 2.56%.

In the case of carbonate gangue minerals, such as calcite and dolomite, separation becomes more difficult to impossible; the difficulty increases with the content in the aforementioned mineral. In such a case, anionic flotation with fatty acid collectors can be used along with modifiers to depress the gangue. Due to this, a lot of lab-scale effort has been devoted to the selective separation of magnesite from carbonates for a long time. In most cases, the tests were performed on pure minerals or artificial mineral mixtures.

Kumlev and Potapenko (1972) separated magnesite from dolomite and calcite by using fatty acids/synthetic aliphatic alcohols mixture as magnesite collector. Sodium carbonate, used as pH regulator, proved to have depressing effect on dolomite, with optimum results obtained in the pH range between 9.5 and 10.5. Sodium hexametaphosphate and NaH₂PO₄ had depressing effect on dolomite as well.

Gallios (1987) studied the anionic flotation using pure magnesite and dolomite minerals and sodium oleate collector; he investigated the effect of the key process parameters, such as conditioning time, flotation time, collector concentration, pH, and water hardness effect. The effect of various modifiers on the flotation of pure minerals as a function of pH was also examined. The reagents tested were sodium pyrophosphate, sodium hexametaphosphate, sodium silicate (Na₂O·xSiO₂), sodium fluorosilicate (Na₂SIF₄), carboxymethylcellulose (CMC), Calgon and 1- (2-hydroxy-1-naphthylazo)-2-naphthol-4-sulphonate (C₃H₇N₂Na₂O₅S). The results showed that these reagents have different effects on the above minerals. All the aforementioned reagents, more or less, depress dolomite flotation in the basic pH range (pH = 7-12), unless sodium silicate that depresses dolomite for pH < 9. Regarding magnesite: a) sodium fluoride, pyrophosphate and hexametaphosphate adversely affect its floatability, with the effect of sodium fluoride being strong while that of the others slight. b) Carboxymethylcellulose and Calgon practically do not affect magnesite. c) Sodium silicate has little activating effect on magnesite. In general, in all cases, the action of the above depressants is stronger on dolomite than on magnesite. Tests on artificial mixtures, in various ratios, have shown that the separation is incomplete due to the interaction of the minerals, despite the encouraging results achieved with pure minerals (Gallios, 1987; Mats and Gallios, 1989).

Chen and Tao (2005) used dodecyl phosphate collector to separate magnesite from dolomite by reverse flotation in the presence of sodium silicate as magnesite depressant. After previous study of the minerals chemistry and its effect on the minerals flotation mechanism, they concluded that the separation is more efficient for 4.5 < pH < 7.5, because in this region sodium silicate selectively precipitates magnesite (Chen and Tao, 2004).

Gence (2006) used pure magnesite and dolomite minerals to study the effect of various depressants on mineral contact angle; the collector used was sodium oleate, alone or along with various depressants such as quebracho, carboxymethylcellulose, or sodium silicate. According to the results, selective flotation of magnesite can be achieved with sodium oleate collector and sodium silicate as dolomite depressant; no further investigation of the minerals floatability was carried out, even on artificial mineral mixtures.

Finely disseminated dolomite is the major gangue of many magnesite deposits in Liaoning Province of China. After very fine grinding of the material (90% less than 0.074mm), Wang and Yang (2010) applied flotation scheme with one rougher and two scavenger stages using SHX collector and sodium hexametaphosphate as a regulator in the neutral pH range. According to the results, they obtained concentrate with yield 72.15% of the initial feed and content 0.71% CaO and 47.1% MgO.

In addition to the traditional anionic collectors used to float carbonates, the microorganism Rhodococcus opacus has been tested and evaluated as bio-collector of magnesite and calcite on bench scale (Casas Botero et al., 2007). The results showed higher affinity of the collector with magnesite, better absorption and higher floatability of magnesite in all tests.

Significant research has been carried out to separate magnesite from silicate and carbonate minerals. A lot of effort has been devoted by Chinese researchers, because of the huge but low-grade magnesite deposits located in Liaoning Province and the necessity to separate these minerals from magnesite.

Li et al. (2010) tried successive flotation stages to separate: a) magnesite from quartz with dodecylamine collector and LM1 (trade name) as a regulator, b) magnesite from dolomite, calcite and quartz with sodium oleate collector for magnesite along with LM2 (trade name) and sodium hexametaphosphate depressants for dolomite and quartz. Sodium carbonate was used as a pH regulator. After investigating the effect of particle size, collectors and modifying reagents, tests were performed at optimum experimental conditions. The results showed that the content of the concentrate in MgO increased from 32.36% to 42.25% while the corresponding in CaO and SiO₂ decreased from 1.08% and 17.7% to 0.19% and 6.73%, respectively; in any case, the recovery of magnesite was not satisfactory.

Han et al. (2013) conducted flotation tests on primary ore from the same region containing magnesite, hematite, calcite, quartz and chlorite with 95.53% MgO, 0.85% SiO₂ and 0.82% Fe₂O₃ content. They used sodium silicate and sodium
hexametaphosphate as depressants and a LKD reagent (amine mixture) as collector; they produced concentrate with improved quality as follows: 0.17% SiO₂, 0.89% Fe₂O₃, and 97.31% MgO while MgO recovery was 78.86%.

Zhu et al. (2014) investigated the possibility to separate silicate minerals and calcite from low-grade magnesite deposit (but with high content of impurities) from Liaoning Province by flotation. The procedure composed of two flotation stages: a) reverse flotation with the novel BK428 anionic collector to remove silica and b) flotation with BK420 cationic collector to remove calcite. This treatment resulted in concentrate production with 47.02% MgO (compare to 43.52% MgO in feed) and 71.64% MgO recovery. Also, the content in impurities was significantly reduced from 3.74% to 0.29% for SiO₂ and from 2.63% to 0.93% for CaO.

Tan et al. (2015) studied the separation of magnesite deposit from another site of the same province of low-grade in magnesite, but high-grade in silicates and dolomite (45.85% MgO, 24.0% SiO₂, and 0.87% CaO) by flotation. The applied flotation circuit aimed at the removal of the gangue minerals (silicates, dolomite) in two stages: a) reverse flotation at pH=7, using waterglass as modifying reagent and the anionic collector BK428 (trade name) and b) second flotation stage for further removal of the gangue using sodium hexametaphosphate as a modifier and BK419B cationic collector. This process produced a concentrate with slightly better MgO content but significantly lower in harmful impurities (46.81% MgO, 0.54% SiO₂ and 0.69% CaO) while magnesite recovery was 80.78%.

Also, Sun et al. (2017) dealt with the removal of silicate and calciferous gangues applying two stages of flotation on finely ground ore (70% < -0.074 mm). In the first stage, a mixture of amine collectors of 150g/t dose was used. The second stage was performed in the basic pH range (adjusted with 800 g/t sodium carbonate) using waterglass and sodium hexametaphosphate mixture with 4:1 ratio (aggregate consumption 600 g/t) and sodium oleate collector (consumption 1200 g/t). Each flotation stage was successively repeated. The content of the concentrate was 46.87% MgO, 0.41% SiO₂ and 0.91% CaO (compare to 41.78% MgO, 4.21% SiO₂ and 3.15% CaO in feed) and the magnesite recovery was 68.21%.

**Separation of Fine Particles**

In many cases, magnesite and gangue minerals (quartz, dolomite) are encountered in microcrystalline form within the deposits; consequently, grinding to fine particle size is required for their liberation. Also, fine particles are generated during grinding, even if the raw material is liberated in coarse size. The fine particles have a multiple adverse effect on the separation by flotation in terms both of value recovery and of selectivity.

Matis et al. (1988) carried out selective separation tests by flotation on magnesite and dolomite of very fine size (45-15 μm). Initially, pure minerals were tested with fatty acids mixture as collector, while the effect of various modifiers such as carboxymethylcellulose (CMC), sodium hexametaphosphate and sodium pyrophosphate was also examined. Subsequently, tests on synthetic mineral mixtures were performed, with encouraging results, especially during the reverse flotation of magnesite.

Yao et al. (2016) investigated the effect of fine magnesite and dolomite particles on quartz removal through reverse flotation. The size of the quartz was relatively coarse (<100 +65 μm), compared to the size of the other minerals. Artificial mixtures, were used as flotation feed throughout the study. The results of the research, on binary mixtures of quartz – magnesite and quartz – dolomite, showed that, at pH = 9 and with dodecylamine collector, the recovery of quartz in the froth was drastically reduced (from 96.66% to 37.15%) for very fine magnesite particle size (<5 μm). Correspondingly, the recovery of quartz (coarser than magnesite) is significantly reduced (from 91.2% to 75.08%), when the percentage of fine (<5 μm) dolomite particle increases from 2.5% to 20%.

Tests were also performed on pure quartz and magnesite minerals to investigate the loss of fine magnesite particles in the tailings of the reverse flotation, with amine as quartz collector (Wang and Sun 2008). The factors studied were the particle size of magnesite and the effect of the regulators KD-1 (trade name of calcium compounds) and of starch. The results showed that size reduction causes a drastic increase in the flotation rate, indicating that magnesite flotation caused by mechanical carry-over. Regarding the effect of the aforementioned reagents, they both cause reduction of magnesite fine particles in the froth for different reasons. KD-1 inhibits magnesite from floating due to viscosity reduction, while starch has a depressing effect on magnesite.

Özkan (2002) studied the effect of ultrasounds on the separation of very fine particles, with size 38μm, from magnesite primary raw ore containing calcite and ferrous clays as gangue. He carried out tests under the following conditions: conventional tests with direct magnesite flotation, ultrasound pre-treatment of the ore prior to flotation, and ultrasound flotation. The reagents used were sodium oleate collector and sodium silicate as depressant. The results showed a slight improvement in MgO content of the concentrate and reduction in harmful ingredients. The more efficient process proved the ultrasonic pre-treatment before flotation.

For very fine particles (-75 +25 μm), Anastassakis (1999) investigated the possibility to separate magnesite from serpentine by selective magnetic coating of the gangue with very fine magnetite particles (-5 μm). From tests on pure minerals, it was concluded that selective coating of serpentine with fine magnetite particles is possible in the pH range 6 < pH < 11, while magnesite is weakly coated for pH > 9. Tests were performed on artificial mixture of minerals, 50% of each, and optimal results were achieved for pH between 6 and 8. Almost all serpentine particles (over 99.5%) acquired magnetic coating and were removed in the magnetic product; the yield of the non-magnetic product (magnesite concentrate) was about 46%, its content in magnesite was higher than 99.5%, and magnesite recovery was 92% to 93%. The same researcher studied the possibility of separating fine magnesite particles from quartz by selective magnetic coating of quartz using pure samples of minerals and magnesite as coating medium (Anastassakis 2002). The results showed that it was possible to separate fine magnesite particles from quartz in the pH range 6 < pH < 11, in the presence of dodecylamine and kerosene. Optimum results were obtained at pH = 8, with the non-magnetic product having a weight recovery of 50.9%, magnesite content 94.1%, and magnesite recovery 95.4%.

Greek researchers (Bimpilas and Anastassakis, 2016) investigated the possibility to separate magnetic gangue minerals (serpentine, ilmenite, and olivine) from magnesite by co-agglomerating all the gangue components and subsequent magnetic separation of the agglomerates. In this respect, hydrophobic agglomeration tests were initially carried out on single minerals, which had been picked-up from the raw ore by hand sorting, to specify the favourable conditions to ensure
selectivity; the most favourable separation was achieved with amine in the basic pH region. Also, the use of non-polar oil improved the results. The results on single minerals were subsequently confirmed by tests on artificial mineral mixtures, as gangue minerals were removed and non-magnetic magnesite concentrates of commercial grade (magnesite content 95% approximately) and of high yield were obtained. Also, Bimpilas (2020) applied the same process to separate magnesite from gangue using primary raw ore. Although the material to be separated had some differences from the single minerals and their artificial mixtures, the results were very promising.

Conclusions

Magnesite ores are of high importance, as they are the major commercial sources of the corresponding commodity, which is used in many industrial and technological applications (e.g. refractories, magnesium metal and alloys production, etc.). The deposits present differences, sometimes considerable, in regard to magnesite mineral crystallinity and gangue composition, which render magnesite separation difficult or impossible in some cases. Even if separation is relatively easy on industrial scale, a great portion of tailings are stacked on piles. These stocks are of relatively high-grade in magnesite, and may be considered as future potential deposits.

The target of the current paper is to review in details the methods applied to separate magnesite from gangue both on industrial and bench scale. Potential processing methods to separate magnesite from gangue minerals of fine particle size are also provided.

References


Sun, Q., Fu, Y., Yao, J., and Li, D., 2017. Experimental study on flotation reducing impurities technique for low-grade magnesite ore from Liaoning Province, Nonferrous Metals (Mineral Processing Section), 2017-05.


EFFICIENCY OF MICROBIAL FUEL CELLS BASED ON THE SULPHATE-REDUCTION BY ETHANOL

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ABSTRACT. The influence of hydraulic retention time (HRT) on the rate of sulphate-reduction and electricity generation of microbial fuel cell fed with ethanol was studied. The experiments were performed in the laboratory installation, consisting of an anaerobic fixed-bed reactor and a microbial fuel cell with air-cathode. An effective sulphate removal was achieved at hydraulic retention times 44 and 66 h. The effectiveness of COD removal raises with increasing the hydraulic retention time. The highest maximum power density of 258 mW/m² was obtained at 22 h HRT. The use of ethanol as an electron donor had a great impact on the composition of the microbial community. The metagenomic data obtained showed that the most abundant phylum in bacterial community was Proteobacteria – 87.8 %, and particularly Gammaproteobacteria – 53.1%. The sulphate reducing bacteria that can incompletely oxidise organic compounds usually with acetate as an end product were presented in the microbial community in anodic chamber. The dominant microbial species among sulphate reducing bacteria was Desulfomicrobium mexicanus (19.7%).

Keywords: Microbial fuel cell, Sulphate reduction, Microbial community, Metagenomic analyses, Wastewater treatment

Introduction

A computational analysis based on a citation network on fuel cells has shown that microbial fuel cells (MFCs) research is of great interest among scientists in recent years (Ogawa et al., 2018). The exponential increase in bioelectrochemical technology research indicates great advancements in this area of knowledge (Gul and Ahmad, 2019). The most significant use of MFCs is the electricity production during the wastewater treatment. In the last years, numerous studies on MFCs based on sulphate-reduction have been carried out (Gao et al., 2014; Miran et al., 2017; Gacítuá et al., 2018). This interest is related to the fact that a major environmental problem in the extraction and processing of mineral resources is the formation of wastewater, containing large concentrations of sulphate. MFCs based on sulphate-reduction have been used for Cu²⁺, Fe²⁺, Pb²⁺, Zn²⁺ and Cd²⁺ removal (Miran et al., 2017; Peng et al., 2016) and metal recovery (Isoasaari and Sillanpää, 2017). The technology has been applied also to organic carbon wastewater treatment (Lee et al., 2014), alcohol distillery wastewater treatment (Ha et al., 2012), diazo dye degradation (Miran et al., 2018).

In most MFCs studies, lactate was added as a carbon and energy source in synthetic wastewaters as it is a preferred electron donor for a large number of sulphate-reducing bacteria (SRB) (Miran et al., 2018; Zhao et al., 2008; Gacítuá et al., 2018). The degree of sulphate’s removal and chemical oxygen demand (COD) depends on a number of factors, the most important of which are pH, temperature, COD/SO₄²⁻ ratio, hydraulic retention time (HRT) (Kousi et al., 2011; Moon et al., 2015). When using lactate as a donor of electrons, during the sulphate reduction, the bacteria produce HCO₃⁻ ions resulting in increase of the pH of the medium. The extent of power density of MFCs based on the sulphate-reduction in conditions of lactate using has been in the range 180 – 680 mW/m² (Lee et al., 2012; Angelov et al., 2013; Gao et al., 2014; Miran et al., 2017). In studies on MFC with SRB consortia and glucose feed solution the amount of power density was much lower - from 9.33 to 39 mW/m² (Niyom et al., 2018; Bratkova et al., 2019). According to Chatterjee et al. (2017) MFC, fed with synthetic wastewater with acetate and COD/sulphate ratio 2.5, could harvest power of 54.4 mW/m².

Few studies have been carried out on MFCs about the electricity production from ethanol (Kim et al., 2007; Song et al., 2005). According to Kim et al. (2007), the maximum power density of the two-chamber MFC was 40±2 mW/m². The same authors reported that when bacteria were transferred into a single-chamber MFC, the maximum power density increased to 488±12 mW/m². It should be noted that in these studies anaerobic sludge from a secondary anaerobic digester was used and the nutrient medium contained a mineral and vitamin solution in phosphate buffer (without sulphate) as well as that the cathode contained a Pt catalyst.

Despite scarce research with ethanol usage in MFCs, it is known that many SRB have the ability to use ethanol as an electron donor (Nagpal et al., 2000). Ethanol has been used as a source of carbon and energy to carry out sulphate-reduction in sulphidogenic bioreactors for mining wastewater treatment (Kaksonen et al., 2004; Bombberg et al., 2017). The stoichiometry of ethanol consumption can be represented by equation (1).

$$2C_2H_5OH + SO_4^{2-} \rightarrow HS^- + 2CH_3COO^- + H^+ + 2H_2O$$ (1)

The effect of different electron donors on microbial community in MFCs was also a subject of many studies in the last years (Sun et al., 2010; Gezginci and Uysal, 2016). As the dominant group of bacterial consortia changed depending on the type of substrate, authors reported different predominant species in bacterial consortia in MFCs. It has been proven that the most common SRB found at the anode area, formed a biofilm in MFCs and fed with lactate belong to the genera Desulfuviibrio, Desulfomicrobium and Desulfobulbus (Miran et al., 2017; Bratkova et al., 2019). It has also been found that SRB consortium reduced the sulphate with a higher rate than the individual single strains (Gacítuá et al., 2018).

The aim of this study was to investigate the performance of MFC and the taxonomic composition of the microbial community in the anodic area of MFCs when using ethanol as an electron donor. The effect of hydraulic retention time on the removal of sulphate and COD has also been studied.
Materials and methods

Design of the laboratory-scaled installation

In order to perform the planned laboratory experiment an installation was constructed, which is presented in Figure 1. The selected design of the laboratory installation consisted of a fixed-bed anaerobic bioreactor where the process of microbial dissimilative sulphate reduction and a MFC with an air-cathode were performed.

![Fig. 1. A laboratory-scaled installation with integrated MFC based on the process of sulphate-reduction: 1 - feeding solution, 2 - peristaltic pump, 3 - anaerobic fixed-bed reactor, 4 - microbial fuel cell with an air-cathode, 5 - recirculation pump, 6 - hydrofoil and a sampling tank, 7 - collector, 8 - load resistance.](image)

The two chambers of the microbial fuel cell were separated with a proton exchange membrane type CMI-7000S (Membrane International Inc.) with an area of 0.0028 m². The two areas were with different volumes, as the anodic was of 0.50 dm³ and the cathodic one - 0.068 dm³. A carbon rod with a surface area of 0.0035 m² (diameter - 8 mm, length - 140 mm) was placed in the anodic chamber as an electrode. A 24 mm layer of pressed activated carbon with particles' fraction size of 2-4 mm was used in the air-cathode chamber. In this layer a graphite rod with a surface area of 0.001 m² (diameter - 8 mm, length - 40 mm) was tucked in.

The anaerobic fixed-bed reactor had a volume of 0.33 dm³. The carrier for the biofilm was solution saturated natural zeolite - clinoptilolite, with a fraction size in the range of 2.5 to 5.0 mm. Its composition is given in a previous research (Angelov et al., 2013). For the saturation of 200 g zeolite 1L of the following solution was used: NH₄Cl – 10 g/l, K₂HPO₄ – 5g/l, MgSO₄.7H₂O – 4g/l. A recirculation pump (5) in an up-flow mode was devised for the homogenisation in the laboratory installation.

Initial cultivation of the consortium of sulphate-reducing bacteria

The anaerobic reactor was inoculated with a consortium of sulphate-reducing bacteria isolated from the fuel element. The culture medium contained 0.25 g/l K₂HPO₄, 0.5 g/l NH₄Cl, 2.0 g/l Na₂SO₄, 0.1 g/l CaCl₂, 4.0 g/l MgSO₄.7H₂O, 8.0 g/l, 6 ml/l ethanol 99%, 0.25 g/l yeast extract, as the pH was adjusted to 7.0. For a period of 2 months a sufficient adherence of the biofilm on the saturated clinoptilolite in the bioreactor was achieved through a periodic replacement of about 70% of the liquid phase after reducing the sulphate concentration to 0.3 g/l with a fresh medium.

Process operation

The laboratory installation was fed continuously with the culture medium after the formation of the SRB biofilm. Different hydraulic retention times (of 13, 17, 22, 26, 33, 44 and 66 h) were maintained for a period of 4 months in order to study the influence of sulphates volume loading rate on the rate of the microbial processes. After reaching a dynamic equilibrium for each mode the effluents from laboratory-scaled installation were sampled repeatedly (3-5 times).

Microbial community analyses

Biomass sample from the anodic chamber of the MFC was taken 4 months after starting the experiment. Then the sample was centrifuged at 12,000 rpm for 10 min, and the supernatant was discarded. The residue obtained was stored at -80°C for further analysis.

Isolation and purification of genomic deoxyribonucleic acid (DNA)

The phenol/chloroform genomic DNA extraction was performed using standard methods (Maniatis et al., 1982). The purification of DNA was conducted with a GFX Genomic Blood DNA Purification Kit (Amersham Biosciences, Piscataway, NJ, USA).

Electrophoretic analyses

In the present study conventional agarose gel (0.7%) electrophoresis was used to separate the total genome DNA. The electrophoresis was run at a voltage varying from 50 to 100 V for approx. 1-2 hours. TBE buffer (0.04M Tris-HCl, 0.04M Boric acid H₃BO₃, 0.002M Ethylenediamine tetraacetic acid, pH 8.0) was applied after 10-fold dilution. The agarose gel with separated fragments DNA was stained with ethidium bromide solution. The fragments were visualised in Benchtop 3UV Transiluminator (UVP, LLC) under UV light (λ = 254 nm). A standard marker 50-3000bp DNA ladder (Sigma Aldrich) for DNA size-determination was used.

Metagenome analyses

After electrophoretic qualitative control, the probe isolated from the microbial biomass DNA and named MGU3 was quantified on Nanodrop. In the present experiment, the concentration of DNA from the MGU3 sample was 69, 98 ng/μl. The probe was processed to construct a library by the amplification of the V3-V4 region of 16S rRNA with specific primers in the laboratory of NGS Macrogen (South Korea). Libraries were sequenced on Illumina HiSeq platforms according to standard protocols. In the current experiments, the protocol included the target sequences with the V3 V4 primer pairs, which created a single amplicon of approximately 598 bp. The identified fragments for 16S RNA were subjected to bioinformatics OTU analysis and grouped into clusters.

Analytical methods

The overall sulphide concentrations were measured with Nanocolor test 1-88/05.09 immediately after the samples from the sampling tank were taken together with parameters as pH, Eh and electrical conductivity (EC). The sulphate contents were measured using a classic spectrophotometric method with BaCl₂. The usage of organic substrate was determined through the measuring of the chemical oxygen demand (COD) and the organic acids and alcohols were determined with a high-performance liquid chromatography. An Aminex HPX-87H
column from Bio-Rad coupled to a RI detector (LC-25RI) was used for HPLC; sulphuric acid (0.01 N) was used as an eluent.

The biofilm that was formed on the used zeolite and graphite in the anodic area after the operation of the installation for 4 months was measured through the Lowry method for protein quantitation.

Samples of the clinoptilolite and the graphite were monitored with a scanning electron microscope (SEM) JEOL/EO VERSION 1.0, and the selected samples were air-dried and gold-coated before the analysis.

The MFC was observed with a digital multimeter Keithley Model 175. A precise potentiometer with maximum value of 11 kΩ was used for the measurements of the external resistances, as during the measuring the external resistance was changed at stable output voltages. The times for reaching steady values of the current and the power were different depending on the external resistance. The geometric anodic surface area was taken into consideration when calculating the power and current densities.

The open circuit voltage (OCV) values for the studied MFC are shown on Fig. 2 and 3. The concentration of sulphate and COD at different HRTs were in the range 658–765 mg/l at HRTs 13, 33 and 66 h, respectively. The maximum sulphate removal (97.9 %) and COD removal (74.8%) were established at a HRT of 66 h. The measured COD values of the outflow were high because of the incomplete oxidation of organic compounds. Data from HPLC analyses showed the incomplete oxidising sulphate-reducer, growing on ethanol, predominate in the microbial community.

Due to the lower pH values, most of the microbial generated hydrogen sulphide was in the form of fully protonated H₂S⁺, a component of gas phase. The concentration of S²⁻ at the outlet of the laboratory installation was determined between 177 and 330 mg/l. The undissociated H₂S is toxic to SRB and the rate of sulphate-reduction and the specific growth rate of SRB correlate inversely to its concentration (Moosa and Harrison, 2006).

COD/sulphate ratio and HRT are the two most important factors for sulphate removal and bioelectricity generation (Zhang et al. 2012). The calculated COD/SO₂⁻ ratio was around 3.25. Data for the rate of sulphate-reduction and sulphate and COD removal are presented in Table 2. We observed that the decrease of HRT from 66 to 13 h led to an increase of the rate of the sulphate-reduction, as the dependence is described by the following equation:

\[ \text{Rate of sulf.-red.} \text{(mg/l/h)} = 808.67 \times \text{HRT}^{-0.6919} \]  \( (R^2 = 0.9977) \)  

(2)

The maximum sulphate removal (97.9 %) and COD removal (74.8%) were established at a HRT of 66 h. The measured COD values of the outflow were high because of the incomplete oxidation of organic compounds. Data from HPLC analyses showed the incomplete oxidise of ethanol to acetate, as the acetate concentration in the effluent were of 0.53, 0.78 and 1.25 g/l at HRTs 13, 33 and 66 h, respectively.

The open circuit voltage (OCV) values for the MFC at different HRTs were in the range 658 – 756 mV. The polarisation and power density curves for the studied MFC are shown on Fig. 2 and 3.
Microbial community results

The population structure and phylogenetic diversity of bacterial community cultured in the anodic area of MFC were studied by metagenomic analysis. The main purpose was to identify the bacterial groups participating in the process of sulphate reduction with the use of ethanol as a source of carbon and energy.

A bioinformatics analysis of the metagenomic data showed that Archaea was virtually absent (0.01%). The identified microorganisms in the studied consortia constitute up to 99.50% and the unidentified microorganisms are a small part - 0.49%. Proteobacteria have the largest part among the identified bacteria - 87.79%, as representatives of Gammaproteobacteria are the predominant, followed by Deltaproteobacteria and Epsilonproteobacteria (Fig. 5).

Most of the Gammaproteobacteria identified in the studied microbial community belonged to the order Pseudomonadales. Deltaproteobacteria include a large number of those known for their ability to reduce sulphur and sulphate bacteria, such as the representatives of genera Desulfuromonas, Desulfovibrio, Desulfobacter, Desulfococcus, Desulfoboche, etc.

The results show that the most significant part of all identified microorganisms in the studied community belongs to the genera Pseudomonas (46.89%) and Desulfovibrio (20.86%). The most common species of the genus Pseudomonas was P. veronii - 43.71%, and of the genus Desulfovibrio – D. mexicanus - 19.79%.

The percentage of sulphate-reducing bacteria was 23.09%, and the total bacteria involved or having a direct effect on sulphate reduction was 32%. The distribution of the species of sulphate-reducing bacteria in the studied microbial community with included carbon source ethanol is shown in Fig.6.

![Fig. 2. Cell voltage in the MFCs as a function of current density at different HRT](image)

The highest maximum power density of 258 mW/m² was obtained at hydraulic retention time of 22 h. At the same HRT the highest concentration of hydrogen sulphide (330 mg/l) was measured. The results obtained are consistent with those reported by other authors which proves that the current produced by the electrodes was dependent on the concentration of the sulphide (Zhao et al., 2008).

![Fig. 3. Power output density in the MFCs as a function of current density at different HRT](image)

![Fig. 4. SEM images of the SRB consortium biofilms on zeolite and graphite (x 6 000) after 4 months; a thin gold layer applied after drying of samples to ensure conductivity. a) Zeolite with biofilm; b) Graphite anode with biofilm](image)

![Fig. 5. Distribution of the classes of proteobacteria in the studied microbial community](image)

![Fig. 6. Distribution of the species of sulphate-reducing bacteria](image)
Desulfovibrio mexicanus is a mesophilic, anaerobic, aerotolerant gram-negative bacterium that reduces sulphate with optimal growth at 37°C and pH 7.2 in a medium containing lactate. It uses also pyruvate, formate, casamino acids, serine, cysteine, H₂ and ethanol as electron donors in the presence of thiosulphate as electron acceptor. Sulphate, elemental sulphur and sulphite also serve as electron acceptors, but not nitrates or fumarate.

Microorganisms, able to reduce elemental sulphur belonging to the genus Sulfurospirillum, organohalide respiratory Epsilonproteobacteria, were found in the studied microbial community. The range of growth substrates includes many toxic compounds, which allows many species of Sulfurospirillum (eg Sulfurospirillum arsenophilum, Sulfurospirillum cavolei) to thrive in contaminated habitats (Goris T. and Diekert G., 2016). In microaerophilic conditions a number of species of the genus Sulfurospirillum could use acetate as a source of carbon and fumarate, pyruvate, lactate, malate, succinate, hydrogen and format as electron donors. The largest presence was registered for the species sulphur-reducing bacteria S. cavolei (4,75%) and S. arsenophilum (4,45%).

The taxonomic diversity of microbial consortia within MFCs changed depending on the type of donor of electrons (Gezginci and Uysal, 2016). The results obtained in our previous studies of microbial communities isolated from the same sulphidogenic bioreactor are comparable, but when using glucose (MGU1) or lactate (MGU2) as a carbon source (Bratkova et al., 2019) will demonstrate significant differences in taxonomic diversity. For instance, the lowest percentage of SRB was detected in the case of cultivation with glucose (3,18%) where D. mexicanus (2,73%) was predominant species. The variety of sulphate reducers is greater when using lactate as an electron donor. The presence of seven such species was detected in anodic area of MFC with a lactate feed solution. They constitute 4,49% of the microorganisms identified in the test sample. Five types of sulphate reducing bacteria have been identified in MGU3, but their total number in the microbial community is more significant (21,46%) and the main part of it is due to D. mexicanus.

Conclusions

In this study, effective sulphate and COD removal with parallel electricity generation were achieved at hydraulic retention times 44 and 66 h by the laboratory installation consisting of an anaerobic fixed-bed reactor and a microbial fuel cell with ethanol as a source of carbon and energy. The highest maximum power density of 258 mW/m² was obtained at hydraulic retention time of 22 h. The anode potential was controlled mainly by the concentration of sulphide. Data received from metagenomic analysis showed that sulphate-reducing and sulphur-reducing bacteria were involved in the transformation of sulphur compounds. The microbial community in anodic chamber contains significant amount SRB that oxidise the organic compounds incompletely with acetate as an end product. The dominant microbial species was identified as Desulfovibrio mexicanus - 19,79%.

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References


SEISMIC EXPLORATIONS FOR DEFINING THE DAMAGE TO THE EARTH DAM PISHICA IN THE REPUBLIC OF NORTH MACEDONIA

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ABSTRACT. The reservoir was built in the middle of the 20th century with a total capacity of 750,000 m³. The height of the dam from the river terrace is 22 m, the length of the crown is 319 m, and the width of the crown is 6 m. Due to the low resistance of the earth dam and the increase of water level due to heavy rains, the lake has leaked on several occasions, causing floods and environmental disaster in the surrounding settlements. Due to heavy rains and overflow through the dam crown, damage to the downstream slope of the dam has occurred and the overall stability of the dam has been compromised. By controlled discharge of the reservoir it is brought to a stable state and the dam breackage is prevented. At the beginning of 2013, the outflow valves of the dam were opened as a result of heavy rains, with reservoir water flowing to more places and residents of the village and livestock evacuated. At the crown of the dam where there was the largest outflow of water, a gap of about 20 m wide and 3.5-4 m thick appeared. Geophysical - seismic surveys have been conducted to determine dam damage.

Keywords: dam, seismic, reflection, refraction, damage

Introduction

The geophysical seismic surveys were conducted according to the Geotechnical Surveys Programme for the repair of the damaged dam, appropriately supplemented with a number of reflective profiles in order to obtain the best possible results for the construction of the dam.

The research was performed using shallow seismic refractive and reflective profiling, with the following purpose:

- Lithophysical breakdown of the body structure and the geological basis of the dam according to values of seismic Vp and Vs velocities;
- Characterisation of the lithophysical media of the terrain and the embedded materials in the body of the dam with values of elastic, dynamic and geotechnical parameters based on the obtained values of seismic velocities;
- Perception of the occurred deformations of the dam and its physical mechanical condition;
- Defining the dynamic characteristics of the dam for the needs of the analysis of its seismic stability. (Slimak, 1996)

The 24-channel ABEM “TERRALOC SEISMIC SYSTEM - MARK 6” (Sweden) was used for the field research, and the ReflexW computer programme was used for the processing and interpretation of the data.

On the basis of the data from engineering-geological and geomechanical research it is obtained that:

- The terrain at the geological base of the dam is composed of andesite tuffs (θ’) which are cracked to compact (θ);
- The body of the dam is composed of sediments (N) represented by dusty sandy clays with the presence of organic matter and carbonates. The dam is homogeneous, with a drainage prism in the base of the downstream slope, without a built-in filter layer of sand and gravel in the body and with a built-in concrete overflow part on the right side. (Delipetrev, 2003)

Seismic explorations

Seismic explorations are performed using refraction and reflection profiles, arranged according to the purpose of the research.

The refraction profiles are made continuously along the entire length of the dam crown, perpendicular to the upstream and downstream slope near borehole D-4, perpendicular to the upstream and downstream slopes in the damaged part of the dam and in the upper part of the upstream slope on the right side. A total of 5 refraction profiles (RF-1 to RF-5) with an overall length of 530 m were constructed. With these studies, a depth of about 25 m has been achieved and the body of the dam, the geological base of the dam and the parts of the sides of the dam under the access roads are covered.

The reflective profiles are also performed continuously along the entire length (except in the damaged part) along the middle of the crown and perpendicular to the upstream and downstream slopes in the damaged part of the dam. A total of 2 reflective profiles with an overall length of 300 m were performed. These surveys cover the body of the dam and the geological base to a depth of about 100 m.

The arrangement of the refractive (RF) and reflective (RL) profiles is shown at the base of the dam (Fig. 1).

The reflective profiles are performed with an arrangement of the geophones at a distance of 5 m from each other, and the seismic waves are excited by 10 kg hammer blows at every 30 m.

The reflective profiles are performed with a geophonic layout of 5 m and with an excitation step of 5 m on the profile RL-1 and 2.5 m on the profile RL-2. For recording the seismic waves, vertical geophones of 14 Hz are used.

Interpretation of refractive profiles

The interpretation is performed using the P and S wave hodohrones, from which the following parameters are determined:

- The values of Vp and Vs seismic velocities of the embedded materials in the dam body and the geological basis;
- Physical - mechanical and dynamic characteristics of the embedded materials in the dam and the geological basis according to the values of the seismic Vp and Vs velocities.

The physical and geological interpretation is shown in the refractive profiles of Figure 1, Figure 2 and Figure 3. It is shown using the P-wave ray paths, except for Figure 2, which also shows the interpretation with S-wave ray path.
The following frame and mean (in parentheses) values of the seismic velocities $V_p$ and $V_s$ of the embedded materials in the dam and its geological basis have been registered with these surveys:

**In the body of the dam:**
- The embankment (dusty sandy clay) in the surface part under the crown of the dam with a thickness of 1.0 - 2.0 m is characterised by values of $V_p = 200 - 365$ (265) m/s and $V_s = 90 - 175$ (115) m/s;
- The embankment (dusty sandy clay) in the surface part of the slopes of the dam with a thickness of 1.0 - 3.0 m is characterised by values of $V_p = 170 - 270$ (220) m/s and $V_s = 80 - 125$ (100) m/s;
- The embankment (dusty sandy clay) in the deeper parts of the dam’s body with a depth of 10 m on the sides up to 23 m in the deepest part of the riverbed is characterised by $V_p = 400 - 565$ (500) m/s and $V_s = 175 - 250$ (215) m/s;
- In the basement of the dam slopes are registered higher values of $V_p$ and $V_s$ ($V_p = 600 - 1400$ m/s and $V_s = 280 - 700$ m/s) than the same in the embankment in the body. These values can refer to the geological environment at the base, and to the downstream slope and to the materials of the supporting prism.
In the geological basement:

- Alluvial sediments represented by fine sand, gravelly to dusty, in places clayey;
- Andesite tuffs, cracked and decomposed on the surface, registered on the sides of the dam, on the surface or under the embankment to a depth of 5 - 15 m with values of Vp = 865 - 1250 (1100) m/s and Vs = 430 - 600 (525) m/s;
- Andesite tuffs, cracked and fragmented within the fault zones to weakly cracked and compact, located at the base of the dam at a depth greater than 10 m, with values of Vp = 2100 - 3250 (2650) m/s and Vs = 1050 - 1650 (1350) m/s;

The values of the seismic velocities in the part of the damaged embankment of the dam are of the same order of magnitude as in the other parts of the body. They indicate that the weakened parts of the embankment have been washed away by the water.

The observed variation of the values of the seismic velocities of the embankment in the body of the dam is a consequence of the uneven compaction of the embedded materials and the changes of the geostatic load which depends on the height and geometric characteristics of the dam (Dragasevic, 1983).

Interpretation of reflective profiles

By interpretation are determined:

- the contact boundary between the embankment embedded in the body of the dam and the geological base,
- information on the achieved compaction of materials in the body of the dam,
- tectonic disturbances and dislocations (faults) in the geological basis.

The obtained results are shown on Figure 5 which shows the interpretation of the reflective profiles RL-1 and RL-2.

The contact boundary between the body of the dam and the geological base is drawn along the longitudinal axis of the dam (along the crown) of the reflective profile RL-1 and along the cross section in the damaged part of the dam on the reflective profile RL - 2. These surveys determine the height of the dam along its entire length. The withdrawn border was also ascertained with the exploration boreholes.

Tectonic faults and crushed zones have been detected in the geological basis of the dam. Along the dam 7 additional locations have been interpreted. Their directions are approximately determined based on the geomorphological characteristics of the terrain. In the zones of these faults in the geological basis lower values of seismic velocities (25-30%) than the obtained velocities in compact tuffs and significantly smaller amplitudes of reflective waves are measured. However, these dislocations are self-indicating and cannot be classified. To determine them, it is necessary to perform parallel reflective profiles on a wider area of the dam site and other appropriate geo-research methods. (Jakosky, 1963)

The interpreted faults are shown on the reflective profiles RL - 1 and RL - 2 (Figure 5).
Conclusion

From the conducted research and obtained data from the seismic reflection and refraction measurements, the following can be concluded:

- The engineering - geological and geomechanical research show that the terrain at the geological base of the dam is composed of andesite tuffs and the body of the dam is composed of sediments represented by dusty sandy clay with the presence of organic matter and carbonates;
- Seismic explorations were performed with refraction and reflection profiles, arranged according to the purpose of the research;
- The following results are obtained by means of the refractive profiles:
  a) in the surface parts of the embankment, the mean values of waves velocity are \( V_p = 220 - 265 \text{ m/s} \) and \( V_s = 100 - 115 \text{ m/s} \);
  b) in the deeper parts of the dam’s body, the mean values are \( V_p = 500 \text{ m/s} \) and \( V_s = 215 \text{ m/s} \);
  c) in the basement of the dam slopes higher values of seismic waves \( V_p = 600 - 1400 \text{ m/s} \) and \( V_s = 280 - 700 \text{ m/s} \) were registered than the same in the embankment in the body. These values can refer to the geological environment at the base, and to the downstream slope and to the materials of the supporting prism.
- The values of the seismic velocities in the part of the damaged embankment of the dam are of the same order of magnitude as in the other parts of the body. They indicate that the weakened parts of the embankment have been washed away by the water.
- By interpretation of the reflective profiles the contact boundary was determined between the embankment embedded in the body of the dam and the geological base and tectonic faults and crushed zones;
- In the zones of the faults in the geological basis lower values of seismic velocities (25-30%) are measured than the obtained velocities in compact tuffs and significantly smaller amplitudes of reflective waves.

References
REVIEW OF THE IRON RECOVERY PROCESSES FROM LADEN LEACH LIQUORS IN HYDROMETALLURGY

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ABSTRACT. Iron is usually present in higher concentrations in the laden solutions and its removal and elimination to a stable phase is a severe problem in hydrometallurgy. This article analyses and compares the processes of solvent extraction and ion exchange as methods for the iron separation and concentration in a sufficient amount, which would enhance its further removal to products with potential for application to other industries. The factors affecting the goethite, hematite and magnetite processes and the area of use of the produced iron oxides are reviewed.

Keywords: iron, processing, hematite, magnetite, hydrometallurgy

Introduction

Iron is the fourth most abundant element in the Earth’s crust, where it exists mainly in four different types of minerals – oxides, sulphides, silicates, and carbonate. The soluble forms of iron are two – ferrous and ferric iron ions as the direction and rate of the relevant oxidation-reduction process strongly depend on the environment’s pH and redox conditions. Ferrous iron is a product of reducing processes, and it oxidises abiotically with high rate at pH above 3.5 in the presence of oxygen, and bacterially at acidic and neutral pH. Some bacterial strains oxidise ferrous iron even at anaerobic conditions. Ferric iron is a product of the oxidation process, its solubility steadily decreases at pH above 3.0, and it precipitates as iron hydroxides. Iron oxides divide into two subgroups – a subgroup of minerals consisting of ferric iron, such as ferrihydrite (Fe₃(OH)₉·nH₂O), goethite (α-FeOOH), hematite (α-Fe₂O₃), for example. The second subgroup of iron oxides consists of ferric and ferrous iron, such as maghemite (Fe₃O₄) and green rust (Fe₃(III)Fe²(II)(OH)₃·nH₂O)₂·nH₂O. Siderite (FeCO₃), typical for sedimentary rocks, and pyrite (FeS₂), found in sedimentary and metamorphic rocks, are examples of iron-containing minerals formed at anaerobic conditions. Because of that minerals variety, it is not surprising that most of the non-ferrous metals (Cu, Ni, Zn) form common sulphides and oxides with iron. As a result, the iron follows the base metals’ route while processing the relevant raw materials. For example, iron (as sulphides) accumulates during the flotation process, and its content in the concentrate can reach up to 29 % (Neale et al., 2009).

Ferric/ ferrous iron plays a crucial role in oxidative/ reductive leaching of secondary sulphide and electronic scrap (Dev et al., 2020) and refractory cobaltic ores and manganese oxides (Das et al., 1982), respectively. The base metal leaches and concentrates in the laden leach liquor, which requires the activities for iron removal and recovery of the valuable element to be applied. Because of higher annual demand of various base metals and rare-earth elements due to the constant growth of the electronic industry, the need for the processing of raw materials and industrial wastes with complex content and mineralogy arises (Chang et al., 2010; Parhi et al., 2015; Georgiev et al., 2018) however, in accordance with strict environmental regulations and applying the principles of the circular economy.

To review the main techniques for the iron removal from laden leach liquors such as solvent extraction, ion exchange, iron precipitation as well as the fate and area of application of produced iron (hydrous) oxides is the main aim of this article.

Precipitation technique

That kind of iron removal technique is based on the direct precipitation of different (hydrous) oxides without the preliminary application of methods for the metal separation to its stream. The main advantage of that approach is the significant simplification of the laden solution flow-sheet and no need to use expensive chemicals, some with toxic properties. It could be applied to two different acidic solutions in which the iron concentration ranges from several hundred milligrams to several dozens gram per litre. Laden leach liquors (LLL) generated from the hydrometallurgical processing of raw materials is the first type of solution to which the approach is applied. The iron concentration can reach several dozens gram per litre in those solutions as the ferrous iron is the dominant valency state. Apart from iron, the substantial concentration of base metals (copper, nickel, zinc), LLL contains silica, sulphates, and aluminium as well. The direct precipitation requires preliminary ferrous iron oxidation combined with a partial acid neutralisation to a specific pH endpoint. Thus, the process is realised in a chemical reactor, and air (in a combination of copper ions as a catalyst), or sulphur dioxide could be used as a chemical oxidant most frequently. The products of the iron removal process strongly depend on the conditions under which the process has been carried out, such as iron oxides with a crystalline structure (goethite (α-FeOOH), akaganeite (β-FeOOH), lepidocrocite (γ-FeOOH), hematite (α-Fe₂O₃), maghemite (γ-Fe₂O₃)) (Wang et al., 2011) or iron hydrous oxides as schwertmannite (Fe₁₀O₁₆(SO₄)₂(OH)₁₂) and ferrihydrite (5Fe₂O₃·9H₂O) with poorly crystalline structure (Loan et al., 2006). In the latter case, the precipitated iron oxides are with low economic value due to the iron content being lower than 50%, and they are usually deposited at sites for long-term storage of technogenic wastes (Table 1). So nowadays, goethite process (Allen et al., 1970; Bodson, 1972), hematite process (Mealey, 1973), para-goethite process (Cubeddu et al., 1986), and zincor process (Meyer et al., 1996) are the main processes applied at an industrial scale, as the latter two are used in the zinc industry only (Loan et al., 2006).

Goethite process

The goethite precipitation proceeds according to the following hydrolysis reaction:
Fe^{3+} + 2H_2O \rightarrow FeOOH + 3H^+(1)

as the ferric iron concentration in the solution must not exceed 1 g/L. The process takes place at a higher temperature (80-90°C) and pH 2-3. Goethite precipitation requires precise monitoring and control between the ferrous iron oxidation (acid-consuming process) and ferric iron precipitation (acid-generating process) as the net reaction is acid generating:

2Fe^{3+} + 1/2O_2 + 3H_2O \rightarrow 2FeOOH + 4H^+(2)

For that reason, both processes are separated into two reactors – a reactor for chemical oxidation of ferrous iron and a reactor for goethite precipitation as the feeding rate of the second reactor is equal to the rate of goethite deposition. Usually, slower precipitation rates are applied because they favour the production of well-crystallised goethite (α-FeOOH) while the higher precipitation rates lead to the formation of akaganeite (β-FeOOH) (Agatzini et al., 1986; Langova et al., 2007). Despite the same chemical formulae, goethite and akaganeite possess a different crystal structure, which has a strong effect on their properties, such as their filtration rate. For example, akaganeite is characterised by a hollandite structure based on body-centred cubic packing of anions. The specific gravity is 3.52 g/cm³ (Cornell and Schwertmann, 2003).

Table 1. The primary type of iron precipitates formed during the iron removal from laded leach liquors of hydrometallurgical processing of zinc concentrate (Onozaki et al., 1986; Piret and Melin, 1993; Ashman, 1996)

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>The technique of iron precipitation</th>
<th>Jarosite</th>
<th>Goethite</th>
<th>Hematite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A:Fe_2(SO_4)_3l(3OH)_4; A=H^+; K^+ or Na^+</td>
<td>α-FeOOH</td>
<td>α-FeOOH</td>
<td>α-FeOOH</td>
</tr>
<tr>
<td>Iron content, %</td>
<td>Theoretical</td>
<td>30-35</td>
<td>62.9</td>
<td>69.9</td>
</tr>
<tr>
<td></td>
<td>Practical</td>
<td>25-30</td>
<td>40-45</td>
<td>50-60</td>
</tr>
<tr>
<td>S content, %</td>
<td>10</td>
<td>5-8</td>
<td>2-5</td>
<td></td>
</tr>
<tr>
<td>Zn content, %</td>
<td>4-6</td>
<td>8</td>
<td>0.5-1.0</td>
<td></td>
</tr>
</tbody>
</table>

Akaganeite is practically unfilterable, and for that reason, its formation as the main product is undesirable at industrial scale operation. Goethite is characterised by an orthorhombic structure based on close packing of anions; the specific gravity is 4.26 g/cm³. Its filtration rate usually is within the range of 80-90 mL/min, and that is also a reason for the broad application of goethite precipitation at an industrial scale (Cohen et al., 2005).

Hematite process

The hematite precipitation proceeds according to the following reaction:

2Fe^{3+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+(3)

This reaction takes place at a higher oxidising environment (pO_2 > 5 bar) and temperatures above 185°C (Ropenack, 1982). Hematite is an iron oxide with deep red colour. It is characterised by a compact crystal structure of corundum type; the specific gravity is 5.26 g/cm³. Its filtration rate varies in the range of 40-130 mL/min, depending on the impurities content (Cornell and Schwertmann, 2003).

The hematite process is carried out in sulphate as well as chloride solutions. However, the exact mechanism of hematite precipitation is quite different. The content of hematite in sulphate media strongly depends on the amount of free sulphuric acid generated during the hydrolysis process. For example, at a temperature higher than 200°C, when the concentration of sulphuric acid reaches the limit of 65 g/L, FeOHSO_4 is the main product of the precipitation process (Umetsu, 1977). At a lower acid concentration, a mixture of FeOHSO_4/Fe_2O_3 obtained. So, the removal of the generated acid, such as neutralisation, controls the way of ferric iron precipitation. The boundary limit of sulphuric acid for hematite formation decreases almost linearly with the temperature decrease at which the process is carried out. The main advantage of the hematite process is that the presence of a higher concentration of base metals (in the range of 60 – 100 g/L) increases the boundary between Fe_2O_3 and FeOHSO_4 to a higher acid concentration at the same temperature.

The hematite precipitation from chloride solutions was studied by Dutrizac and Riveros (1999) at temperatures below 100°C, ambient pressure and in combination with seedling. The researchers proposed two different mechanisms of hematite formation. The first mechanism took place at 100°C without seeding with Fe_2O_3, and akaganeite (β-FeOOH) was the product of iron precipitation. However, akaganeite is a metastable phase at those conditions, and it transforms into hematite at a prolonged time. Iron precipitates to hematite directly when the process takes place at a lower temperature (60°C) and the seeding rate is in the range of 10-20 g/L. The percentage of iron removal is almost 100%. Temperature and pH have a substantial effect on the precipitates colour and filtration (Masambi et al., 2016). The deepest red colour, typical of hematite, is produced at lower pH (1.0) and higher temperature (80°C). Increasing the pH and decreasing the temperature lead to precipitates with substantial brown colour with an insufficient pigmentary characteristic. However, the filtration rate improves in the same direction due to the reduced zeta potential of fine particles and further agglomeration.

The higher iron content (Table 1), chemical stability and density of hematite qualify it as a by-product that can be used as a raw material for the production of iron, steel, or pigments according to the impurity content (Masambi et al., 2016).

Paragoethite process

Despite its name, this process is carried out at conditions completely different from conditions at which the goethite process takes place. For example, the ferric iron concentration is in the range of 12-16 g/L; the temperature is in the range of 80 – 85°C, the initial pH is 1.0, while the final pH is 3.5. Not surprisingly, ferrihydrite (Fe_2(OH)_3·4H_2O and schwertmannite [Fe_2O_3(3OH)·SO_4] are the main iron phases formed at those conditions (Loan et al., 2006):

8Fe^{3+} + 14H_2O + H_2SO_4 \rightarrow Fe_2O_3(3OH)·SO_4 + 24H^+(4)

Besides these two minerals, jarosite, silica, and poorly crystalline goethite are also detected (Claassen et al., 2002). Schwertmannite and ferrihydrite are characterised by brownish-yellow to dark brown colour and very similar specific gravity (3.77 – 3.95 g/cm³) (Cornell and Schwertmann, 2003). The main advantage of that iron removal process is the higher rate of laded leach liquor processing with no strict limits about the ferric iron concentration. Thus, the process is applied in the
The process of iron hydrolysis/precipitation and ferric iron hydrous oxides formation combines with sorption or co-precipitation of other pollutants contained in mine waters (such as sulphate, aluminium, toxic elements, and some amount of non-ferrous metals). The endpoint of pH neutralisation and the molar ratio between iron and other pollutants are the key factors that control the rate and extent of sorption/co-precipitation processes. For example, the iron precipitates as goethite, mainly when the endpoint of pH neutralisation is lower than 5.0 (Fish et al., 1996) with minimal co-precipitation of silica and gypsum. The generated rich-in-iron-sludge (the content of iron oxides is higher than 50%) is with satisfactory pigmentary characteristics, and it is used as a raw material for the production of mineral pigments for industry (Hedin et al., 2002). If the endpoint of pH neutralisation of AMW is above 5.5, the generated rich-in-iron-sludge is with weak pigmentary characteristics due to the less than 50% content of iron oxides. It requires their removal periodically from the passive system and long-term storage at a tailing.

**Magnetite process**

Magnetite is an iron oxide with black colour characterized by an inverse spinel structure and ferrimagnetic properties due to the presence of ferrous and ferric iron in its structure. Its specific gravity is 5.18 g/cm³ (Cornell and Schwertmann, 2003). The magnetite precipitation proceeds according to the following reaction:

$$\text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- \rightarrow 4\text{H}_2\text{O} + \text{Fe}_3\text{O}_4 (\text{Fe}_4\text{Fe}_5\text{O}_8)$$  \(\text{(5)}\)

The process takes place in alkaline pH (9-11), atmospheric pressure, and temperature in the range of 60 – 100°C (Rabelo et al., 2001; Jolivet et al., 2004). Thus, the magnetite process is suitable only for rich-in-iron technogenic solutions with acidic pH, which are generated after the preliminary iron separation and concentration from the other components of laden leach liquor through an ion exchange resin/solvent extraction technique. Anaerobic conditions are obligatory, as well as the accurate monitoring and control of the ferrous oxidation enabling the maintenance of the exact ratio between ferrous to ferric iron (2:1) in the reactor. The average size of the obtained magnetite nanoparticles ranges between 10-15 nm up to 25-30 nm (Wei & Viadero, 2007; Zhang et al., 2015). Their form is cubic or spheroidal. Magnetite nanoparticles find applications in biomedicine, nano-sorbents and environmental engineering, controlled drug delivery, and ferrofluid technology (Gupta and Wells, 2004; Mak and Chen, 2004; Love et al., 2005).

**2. Techniques for separation and concentration of iron from LLL before the application of precipitation methods**

The development and applicability of hydrometallurgical methods at an industrial scale depend on the presence of effective methods for separation and concentration of base metals from laden leach liquors. The process of cementation on the surface of zero-valent metal was widely applied into the practice at the beginning (Ahmed et al., 2011). Over the years, it has been replaced by processes of ion exchange and solvent extraction. Both alternatives are based on using highly selective reagents towards relevant elements, which react at higher rates in both directions - the processes of concentration and elution (stripping) of ion exchange resin or organic solvent, respectively.
As a result, the methods of ion exchange and solvent extraction have had a strong positive effect on the further development of hydrometallurgy, and its application in the processing of a wide range of raw materials (ores, concentrates, technogenic wastes or electronic scrap) enriched not only with non-ferrous metals but also with rare earth elements.

Ion exchange processes

The chelating ion exchange resins suitable for iron ion exchange are divided into five main classes according to their chemical content: iminodiacetic, picolylamine, sulphonated diphosphonic, sulphonated phosphonic, and aminophosphonic. All these classes have a stronger affinity to ferric iron in comparison to the ferrous iron form (McKeVitt and Dreisinger, 2009).

The phosphonic acid group (PO₃H₂) based on chelating ion exchange resins are widely used in practice and are known under the trade names LEWATIT (Guide, 2012), Purolite (Lenntech), and Dyphonic (Chiarizia et al., 1997). Their most important advantage is the high degree of selectivity to iron because of the complexes formed between the resin’s reactive part and ferric iron (a stage of loading), instead of just ionic bond, and its capability of complete regeneration (a stage of elution). This method applies to technogenic solutions laden with higher concentrations of valuable ions as copper, cobalt or nickel (Lee and Nicol, 2007; McKeVitt and Dreisinger, 2009).

The reaction between the protonated form of the phosphonic group and ferric iron proceeds according to this equation:

\[ \text{Fe}^{3+} + 3(\text{HR}) \rightarrow \text{FeR}^2 + 3\text{H}^+ \]  

Temperature, pH, acidity concentration or the type of ion exchange resin have a substantial effect on the iron adsorption, and their impact is studied using batch and continuous flow experiments. The parameters determined by batch tests are:

1. The total amount of iron adsorbed by the resin at equilibrium, qₑ (in mg/g resin), i.e. the state at which the whole resins adsorption capacity is exhausted;
2. Percentage of iron removed from laden leach liquor due to adsorption by the chelating resin, S (in %);
3. Distribution coefficient, i.e. effectiveness of ion exchange resin to remove and adsorb a particular ion from the solution, \( K_d \);
4. The separation factor that describes preferences of resin to iron in contrast to each base metal from the processed liquor, i.e. a ratio of iron-loaded to each base metal loaded.

For example, the experiments carried out by Izadi et al., (2017) revealed that the maximum adsorption capacity of Purolite S957 to iron from industrial copper raffinate solutions was 42 mg Fe/g resin. The equation rate with pseudo-\( n \)-th order and Langmuir-Freundlich model predicted the kinetics and equilibrium data of the ion exchange process.

The parameters determined by continuous flow experiments (fixed bed studies) are:

1. The efficiency of column adsorption at the tested flow rate, %;
2. Breakthrough time, i.e. the time needed for the resin surface’s saturation so that the outlet iron concentration of column becomes 0.3 % of the inlet.

The adsorbed iron eluted completely at acidic pH, which regenerates the initial resin’s adsorption capacity. So, the metal separates and concentrates in a separate technogenic stream, a precondition for the iron recovery to products applicable for other industries. The elution process can be carried out with sulphuric or hydrochloric acid according to the pH and the method for iron precipitation. However, in both cases, acid consumption is significant, and it ranges between 5 – 7 g acid/g resin depending on the type of resin and the experimental conditions at which the process takes place (Zhang et al., 2016; Izadi et al., 2017). The regeneration stage could be carried out in the presence of a suitable reducing agent (SO₂, CO or oxalic acid for example) which reduces ferric iron to ferrous state as the latter liberates quickly from the resin’s surface at slightly acidic pH (Lee and Nicol, 2007; Zhang et al., 2016). So, acid consumption could be reduced significantly, which is a significant advantage for those cases where the precipitation is carried out at highly alkaline pH.

Solvent extraction process

This is the second option that is used to separate and concentrate iron in its stream before its recovery as the relevant iron (hydrous) oxide. The process is carried out in two stages – extraction and stripping. The extraction stage relies on a mixture of appropriate diluents (such as kerosene, toluene, xylene or n-octane) and a suitable organic compound, mostly organophosphorus acids, which form a strong bond with ferric iron from leach liquor. Among the organophosphorus acids, D2EHPA ((di-2-ethylhexyl) phosphoric acid) is the most widely used. Because of the acidic properties, the extraction ability of D2EHPA strongly depends on the extent of preliminary neutralisation with NaOH. Apart from iron, some base metals, zinc mostly, are co-extracted too (Azizorhaben et al., 2016), as the experimental conditions (concentration, organic to aqueous phase ratio and pH) affect the process’s rate. The efficiency of solvent extraction (E, %) and the distribution coefficient between the two phases (D) describe the removal of each metal. The separation factor (β) between iron and the co-extracted base metal describes the reagent selectivity at the relevant experimental conditions. For example, the lower value of \( \text{pH}_{\text{equilibrium}} \) (in the range of 0.9 – 1.1) increases the amount of the extracted ferric iron on account of zinc, which affects the value of separation factor (\( \beta_{\text{Fe/Zn}} \)) (Georgiev et al., 2018).

The main drawback of using D2EHPA as a ferric iron extractant is the need for a highly acidic solution (such as 5 – 6 M) for the stripping stage. It has a substantial limitation for further processing of the rich-in-iron stream. The preliminary reduction of ferric iron to ferrous state is the option to carry out the iron stripping in a slightly acidic solution (0.07 – 0.15 N). Oxalic acid (Akhlaghi et al., 2010), molecular hydrogen (Demopoulos, G., Gelvert, D. 1984), and some metals in zero valency state (galvanic reduction) (Chang et al., 1996; Sun and O’Keefe, 2002) are the most studied reducing compounds for that purpose.

Conclusions

Processing of raw materials with complex chemical content and mineralogy, stricter environmental regulations and ideas of the circular economy are the factors that set the growing role of the ion exchange and solvent extraction in iron recovery from laden leach liquors. Both methods produce rich-in-iron technogenic solutions, making possible iron oxides with preliminary fixed characteristics to be generated with the relevant iron precipitation technique application.
References


Azizorghabegi, A., Rashchi, F., Babakhani, A., 2016. Stoichiometry and structural studies of Fe(III) and Zn (II) solvent extraction using D2EHPA/TBP. Separation and Purification Technology 171, 197–205.


Guide. 2012. Portfolio of Lewatit® ion exchange resins. LANXESS Deutschland GmbH.


LennTech Water Treatment Solutions. Mining Industry.


LABORATORY MODEL OF A MAGNETIC LEVITATION SYSTEM

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ABSTRACT. The magnetic levitation consists of balancing the forces of attraction and repulsion of a ferromagnetic object located in a foreign magnetic field in such a way as to keep a desired distance between the object and the magnet. This technology is receiving increasing attention because it helps to eliminate the frictional losses due to the lack of mechanical contact. This makes it possible to reduce the wear of critical machine parts and achieve high speeds with increased positioning accuracy. Advanced applications include the high-speed Maglev trains, magnetic bearings and suspension, electromagnetic cranes, high-accuracy positioning of wafers in photolithography in the manufacturing of integrated circuits, and other high-precision contactless positioning devices. Positive results are also observed in applications from the mining and processing industry in the extraction and processing of raw materials, which makes the topic relevant. The paper presents a laboratory model of a single degree of freedom electromagnet-based system intended to aid the studying of the effect of magnetic levitation. The possibilities for the implementation of different positional feedback types are discussed together with the power circuit that drives the electromagnet. A mathematical model and implementation of a fully digital algorithm that uses the PID control law are presented. Experiments are conducted that could aid in building a sensorless control system. The elaborated laboratory model allows for easy upgrade and can be used in disciplines in the field of measurement, control, and automation as a whole.

Keywords: Magnetic Levitation, Pulse Width Modulation, Programmable Logic Device, Processing of Raw Materials

Introduction

The levitation is a way of lifting and suspending an object in the air without physical support and contact with the ground or other objects. To overcome the gravitational force of attraction, it is necessary to create a counteracting force that is large enough to lift the object. Next, a control algorithm is needed to achieve a stable equilibrium that keeps the object at the desired distance. Various types of creating levitation exist based on the nature of the occurrence of the counteracting force such as electrostatic levitation, aerodynamic levitation, acoustic, optical, and magnetic levitation to name a few. What they have in common is the lack of physical contact between the object and its environment and therefore the lack of friction and wearing. In addition they eliminate lubricants that can be a source of contamination. All of the above is of extreme benefit for linearly or rotational moving devices that pave the way for the myriad applications of the levitation (Yaghoubi, 2013) such as the Maglev train with either servo-stabilised electromagnetic suspension (EMS) or electrodynamic suspension (EDS) (Vuchic, 2002; Hyung et al., 2006), wind turbines (Manoj, 2019), frictionless magnetic bearings (Hiroyuki, 2000, Qiao, 2020), magnetic separation of raw materials (Alexandrov, 2013; Peng, 2018), aerospace engineering like the launch ring (McNab, 2003; Hull, 2007), medical applications like the blood pump (Wang, 2016), etc. Research is also being done to use the magnetic levitation technology for contactless, high-precision positioning of wafers in photolithography (Lahdo, 2016).

In the field of education many companies exist such as Quanser (Quanser, 2019), Inteco (Inteco, 2005), Feedback Instruments (Feedback Instruments, 2019) and others that offer lab-ready kits but they are expensive and are often associated with the use of commercial software such as Matlab in combination with proprietary hardware. Therefore, this paper presents a laboratory model of a Magnetic Levitation System (MLS) built at the University of Mining and Geology “St. Ivan Rilski”. It represents a single degree of freedom MLS that allows for levitating a hollow metallic ball vertically up and down. The platform can be easily extended to conduct various experiments and do research in the field of magnetic levitation and control systems.

Essence of the problem

The basic working principle of the laboratory model is depicted in Fig. 1. It helps to reveal the control goal of the system which consists of supporting a hollow steel ball in the air at a desired distance apart from an electromagnet.

![Fig. 1. Working principle of the magnetic levitation plant](image)

The system consists of a controller (CTRL) which applies pulse width modulated signal (PWM) to the power stage (PWR) to control the current \( I_c \) through the coil of the electromagnet. This current can be calculated by measuring the voltage drop \( V_s \) across the current sense resistor \( R_s \). In the figure the coil is presented with its active resistance \( R_c \) and its inductance \( L_c \). The electromagnet generates an electromagnetic force \( F_e \) which counteracts the force of gravity \( F_g \). The hollow steel sphere is placed along the vertical axis of the electromagnet at some distance (air gap) \( \delta \) apart from it. The size of the air gap is measured with the aid of the sensor \( S \) and is fed back to the controller which algorithm calculates and adjusts the new PWM value.

The mathematical description can be done by writing the equations for the voltage and the mechanical part of the circuit. It should be noted that the electrical subsystem is much faster...
than the mechanical subsystem. The coil current can be computed using the relationship (1):

\[ V_c(t) = R_s i_c(t) \]  

(1)

Using the Kirchhoff’s law the following first-order equation can be derived (2):

\[ V_c(t) = (R_s + R_g) i_c(t) + L_c \frac{di_c(t)}{dt} \]  

(2)

The force that is experienced by the ferromagnetic sphere is given by the fundamental principle of dynamics – the second Newton’s law of motion (3):

\[ F_R = F_g - m \cdot g \cdot k \left( \frac{i_c(t)}{\delta} \right)^2 \]  

(3)

Where \( F_R \) is the resultant force, \( m \) is the ball mass, \( g \) is the gravity force and \( k \) is the magnetic force constant for the electromagnet-ball pair. In order for the ball to levitate in the air it is necessary to reach the condition of equilibrium (4):

\[ F_R = F_g - m \cdot g \cdot k \left( \frac{i_c(t)}{\delta} \right)^2 \]  

(4)

Solving for the current gives (5) which allows to obtain the current value as a function of the air gap \( \delta \).

\[ i_c(t) = \sqrt{\frac{m \cdot g}{k \cdot \delta^2}} \]  

(5)

The influence of the air gap over the force produced by the electromagnet \( F_c \) can be plotted by solving (6).

\[ F_c = (n \cdot i_c(t))^2 \cdot k \cdot \frac{s}{\delta^2} \]  

(6)

In this equation \( n \) is the number of turns in the coil and \( s \) is the area. The 3D plot for \( F_c \) as a function of the current and the air gap is shown in Fig. 2.

![Fig. 2. Three-dimensional plot for \( F_c \) \( (I, \delta) \)](image)

As can be seen, the function is highly nonlinear. Given these data it becomes obvious that the distance can be controlled over a narrow range of about 0 to 2 cm depending on the properties of the ferromagnetic object. The near to zero distance is of no practical interest since the precision and dynamics of the control at very small air gaps are limited by the saturation conditions.

**Feedback sensor types**

In order to levitate the ferromagnetic object in the space a good estimation of the size of the air gap is needed. Many types of distance feedback techniques exist that are appropriate for this MLS laboratory model. They can be classified as passive or active, by the nature of the signal they emit (if any) or by their working principle. Some of the most popular sensors are discussed briefly below.

**Photoelectric sensors**

The family of the photoelectric sensors includes any pair of light-emitting and photodetector devices but the infrared (IR) and laser-based sensors are most common because they are less sensitive to the daylight spectrum. Two effects can be used here – the reflection from the target or the beam intersection. The most common case is to mount an optocouple split between both the vertical columns of the MLS frame. This way the levitating object intersects the light beam by either reducing the light intensity falling on the receiver or interrupting one or more light beams in the case where the sensor is in the form of an array. The other possibility is to use a distance measurement reflective isotropic position sensitive device (PSD) like the Sharp GP2D12 or a laser ranging sensor such as the ST VL53L0X. The first one is a non-monotonic transducer which means that its static characteristics have no inversion so that it is not applicable for small distances because the readings may be ambiguous. The second one employs the time-of-flight (ToF) principle but it is pricey and poses higher requirements for mounting precision. Both the Sharp and the ST sensors are sensitive to the colour of the object and its diffusing properties.

**Acoustic sensors**

The acoustic sensors are usually ultrasonic devices like the HC-SR04 transducer. They are active sensors that emit high frequency sound wave to the object and calculate the time it takes for the reflected sound wave to get back to the receiver. This principle is called the time-of-flight (ToF) and is given in (7):

\[ d = \frac{t \cdot \nu}{2} \]  

(7)

Where \( d \) is the distance to the object, \( t \) is the time for the wave to get to and back from the object and \( \nu \) is the speed of sound in the medium (the air) which is slightly dependent on the temperature. This sensor can be mounted under the object but it does not cope well with its spherical shape – the ball, and is mostly suitable for higher distance ranges as its measurement accuracy is relatively low.

**Capacitive sensors**

The capacitive sensors can detect both ferromagnetic and non-ferromagnetic targets. Their principle of operation is based on the use of two conduction plates at different potentials with little capacitance between them, that are linked to an oscillator, and a frequency counter. The air acts as an insulator and the object alters the capacitance thus changing the oscillator frequency. The capacitive sensors are moisture sensitive devices so the room conditions may impede their readings. They can be mounted under the ferromagnetic ball but their linearity and sensitivity is not good enough for the purpose of the current MLS.
Magnetosensitive sensors

There exist two major categories of magnetosensitive devices which are based on two galvanomagnetic effects – the Gaussian effect and the Hall effect.

The first category covers the magnetoresistive sensors where the active resistance R depends on the induction B of the magnetic field. This category in turn includes the anisotropic magnetoresistive sensors (AMR) and the giant magnetoresistive sensors (GMR) which are commercially available. The GMR effect was discovered relatively soon (1988) and its discovery was awarded the 2007 Nobel prize in physics.

The second category covers the Hall effect sensors. The essence of the Hall effect is that if a current carrying conductor is placed in a magnetic field with magnetic induction, perpendicular to the current, then an electric field emerges in that conductor in a direction which is perpendicular to both the current and the induction. This field creates a transverse potential difference called the Hall voltage. The proposed MLS employs the continuous-time linear Hall effect sensor A1302 by Allegro Microsystems. Its low price, small size, high sensitivity of 1.3 mV/G and high linearity emphasises its advantages over other sensors. The generalised dimensionless transfer characteristics of this type of sensors are depicted in Fig. 3 (Pepka, 2013).

![Fig. 3. Transfer characteristics of A1302 throughout the range of sensed magnet flux, courtesy of Allegro (Pepka, 2013)](image)

It can be seen in the figure that the characteristic is quite linear and there are two saturation areas which limit the minimum and maximum voltage. Since the hollow ferromagnetic ball acts as a ferromagnetic concentrator of the magnetic flux the output voltage is in proportion with the size of the air gap which is linearised by the integrated circuit (IC).

The construction of the proposed laboratory model allows for any type of feedback sensor to be easily mounted onto the frame.

Power stage circuit

Although a simplified solution like a discrete MOSFET transistor is appropriate here, a dedicated fully integrated H-bridge driver is used to power the electromagnet. This is the ST VNH5019 based Arduino shield from Pololu (2019). The block diagram of the power stage is shown in Fig. 4.

![Fig. 4. Block diagram of the VNH5019](image)

The electromagnet coil is connected between the OUTa and OUTb leads of the integrated circuit. The n-type MOSFET transistors HSa, LSa, HSB and LSB form a full bridge that is capable of four-quadrant operation and can provide current of up to 30A. The VNH5019 IC is chosen because it supports protective functions such as undervoltage, overvoltage and thermal shutdown, cross-conduction protection and current limitation which are invaluable for the experimental MLS platform. Additional advantage is the provided current sense capability which allows for measuring the current through the coil.

Control algorithm

Because the electromagnetic levitation system described in this paper is intended to be used mainly for teaching, a universal proportional-integral-derivative (PID) control algorithm is implemented. It is a closed-loop feedback system subjected to the three-component control law (8):

\[ u(t) = k_P e(t) + k_I \int_0^t e(\tau)d\tau + k_D \frac{de(t)}{dt} \]  

(8)

Where \( u(t) \) is the control signal, \( e(t) \) is the error derived by subtracting the real position from the setpoint, and \( k_P, k_I, k_D \) are the tuning parameters for the corresponding gains.

The proportional (P) term alters the control variable proportional to the loop error and it takes effect instantly. The integral (I) term alters the control variable proportional to the loop error and its course over time. It does not work instantly, but it is able to fully minimize the loop error. The derivative (D) term has to do with how fast the error changes. By manipulating each of the \( k_P, k_I, \) and \( k_D \) parameters the responsiveness and the stability of the control loop can be examined.

The general block diagram of the implemented closed-loop MLS system is shown in Fig. 5. The plant is directly driven by the power amplifier (Power Shield) which input is taken from the PWM output stage of the Arduino controller. The plant is covered by a negative feedback in a closed-loop control system. Its behaviour is being measured by the Hall effect sensor and the result is read by the analogue-to-digital (ADC) converter of the controller. The assignment (setpoint) and the control gains are set by the personal computer which connects to the controller via serial (USB) link.
and the size of the air gap. The measurements were taken by fixing the hollow sphere by the aid of a screw metal stud at a distance of 0 to 25 mm with a step of 1.25 mm. Next, by measuring the voltage \( u \) and the current \( i \) and by knowing the active resistance \( R \) the flux can be calculated by solving (9):

\[
\psi(t) = \int \left( u(t) - i(t) \cdot R \right) dt
\]

The experimental setup for this measurement is shown in Fig. 7(a) and the family of flux linkage curves is shown in Fig. 7(b).

\[\text{Fig. 7. Setup for measuring the flux linkage (a), and the family of flux linkage curves (b)}\]

The bottom curve in Fig. 7(b) corresponds to the farthest distance, i.e. the one where no saturation is observed because of the minimum inductance. The top curve corresponds to the minimum air gap where the inductance is maximized. It can be seen in the figure that the bottom adjacent curves are very close to each other. That means that a small error in the flux linkage will result in a large error in the distance estimation which will reduce the accuracy. This statement covers the observations made for Fig. 2.

The measurement data can be entered into a look-up table (LUT) as shown in Fig. 8.

\[\text{Fig. 8. Air gap estimation by measuring the voltage and the current}\]

The fact is that the actual air gap value can be estimated by only measuring the voltage and the current can help in implementing a sensorless control MLS, thus fully eliminating the distance sensor. In order to make this algorithm possible, it is necessary to do preprocessing of the incoming data, expressed mostly in digital filtering in real time. That means that a faster controller may be needed. Also the look-up table is to be prepared in advance.

\[\text{Future work}\]

Although the presented laboratory model of a magnetic levitation system is complete and fully operational, there is a wide field for future work. Some of the ideas include:

- Eliminating the feedback sensor by finishing the air gap estimation algorithm, based on (9);
• Finding a suitable faster microcontroller. A possible solution is to use the much more powerful Teensy board that is based on the Arm Cortex-M CPU or even a small field programmable gate array (FPGA). A very good candidate in this regard is the Alorium Technology XLR8 board that includes a fully compatible Arduino core and a free reconfigurable fabric both embedded into a single Intel MAX 10 FPGA device;
• Adding a small display and rotary encoders for manually setting the tuning coefficients that will make the laboratory model a self-contained device;
• Extending the firmware to support direct communication with mathematical packages such as the free SciLab software. This will allow to deploy complex mathematical models in a hardware-in-the-loop (HIL) configuration.

The idea of enabling the proposed setup for remote access also exists thus ensuring that the device will be ready for distance learning. This step will require some additional mechanical components in order to prevent the ball from falling out and some firmware modifications that should provide a reliable way for restoring the system in the initial state.

Conclusions
The magnetic levitation technology makes it possible to eliminate friction and reduce wear of critical machine parts, which aids in achieving very high speeds without loss in applications such as the magnetic levitation trains and many others, which determines the increasing attention by the industry. Together with the increasing accessibility and computing capabilities of the hardware, this makes the topic relevant and mandatory for study in automatic control courses.

This paper presents a laboratory model of a single degree of freedom magnetic levitation system built at the University of Mining and Geology „St. Ivan Rilski”. The principle of operation and the mathematical description are introduced together with the feedback types, the power stage and the mathematical description are introduced together with a possible digital implementation of the control algorithm. The research is supported by a physical experiment that proves the operability of the system. A way to implement sensorless control is suggested, which is also supported by a physical experiment. The built system allows upgrading and opens a broad field for research.

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References
RATIONALISING THE LOCATION AND DESIGN OF THE WASTE DUMP IN THE CASE OF OPEN-PIT MINING

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ABSTRACT. The location for dumping the waste from the open-pit mine has a significant weight for the establishment of the waste treatment costs. According to the constructive parameters of the waste dump and the terrain’s characteristics, the volume of the affected area is determined, in relation to the waste volume generated from the exploitation of a mineral deposit. In order to optimise the waste dump’s location and its constructive parameters, a number of alternatives have to be taken into account. These alternatives have to be technically plausible, as well as their safety factor must be satisfactory. Based on the considered alternatives, the optimisation problem can be defined so that the optimal solution provides the required capacity of the waste dump, as well as a minimal area of negative environmental impact and lowest operational costs.

Keywords: waste dump, optimisation, location, costs

Introduction

Waste dumping of the overburden in open-pit mining tends to be a topical problem all around the world due to the long term impact on the environment. In order to ensure a suitable site for waste (overburden) dumping, certain areas have to be obtained from the state or from their private owners. These areas are usually either forested, fertile lands (sometimes used for agricultural purposes) or infertile lands. Nevertheless, due to the accelerated environmental policy on a world-wide scale and the intense growth of the responsibilities which mining companies have to take, the overburden treatment problem tends to be more complex than decades ago. Undoubtedly, the negative environmental impact from waste dumping has to be minimal. At the same time the operational costs for waste dumps building have to be minimal too which sometimes conflicts with the minimal environmental impact goal. Therefore, a certain balance has to be achieved in order to satisfy the specific environmental requirements for the region, where the open-pit mining takes place, as well as to minimise the transportation costs, operational costs for waste treatment (Aleksandrova, 1998) and their respective auxiliary operations costs.

Analyses show that during the exploitation of a certain deposit the overall costs for overburden treatment tend to be approximately 10 – 12% from the total operational costs for open-pit mining (Atanasov et al., 2001). Therefore, optimising this group of operational costs will lead to an increased profit for the mining companies. Due to the improved capabilities of mining software products and their options for automated waste dump designs, many design alternatives can be generated for a shorter time, which would lead to more rational and reasonable decisions when choosing the final waste dump design. This could lead not only to the improvement of the economic impact of the waste dumping, but the scale of waste dumping as well and therefore the scale of the environmental impact.

Rationalising the waste dumping solution

Let there be N considered alternatives for areas, where the overburden from the open-pit mine could be dumped. These areas have to be considered according to the specific terrain inside the claimed area, acquired from the state. An alternative which is considered feasible is the one which follows each of these key requirements:

1) it is not placed outside the claimed area from the mining company;
2) it is not placed on areas, which will compromise the environment’s water sources;
3) it is not placed on weak soil which will compromise the dump stability;
4) it is not placed near roads and buildings, which may become compromised.

Depending on the type of extracted mineral resource, further conditions may be adopted as well. Nonetheless, every feasible area for waste dumping can vary depending on their rationality. The most rational places where waste dumping can take place are concave land forms, due to the improved stability of the dump as well as their ability to accumulate higher amounts of waste volume. Plain terrain could also be used for waste dumping due to its easy access. Convex land forms also prove to be feasible for waste dumping, however, the terrain slope has to be considered carefully. In addition, hillside dumping may prove to ensure the stability of the waste dump, it also reduces the overall volume the dump could accumulate (Atanasov et al., 2001).

Therefore, the N considered dump areas alternatives can include convex, concave land forms or plain terrain (natural and artificial) which fulfil all the environmental and legal requirements of the state. Each considered dump area can accumulate a certain amount of waste depending on the waste dump design.

In order to minimise the negative environmental impact, the total area used for waste dumping has to be minimal (Aleksandrova, 1999). This leads to several benefits – no additional forested or fertile areas have to disturbed, as well as no further reclamation activities have to be made. From an economic point of view, waste dumping depends mostly on the distance of the dump from the open-pit mine and therefore an optimisation problem must be solved for the transportation costs (Ortiz, 2017).

In order to achieve a balance between the environmental impact of waste dumping process as well as the economic feasibility of the dump design, two target functions are defined:
\[ F_1 = \sum_{i}^{N} C_{dis} + C_{tr} + C_{ci} + C_{rec} \rightarrow \min \]  
\[ F_2 = \sum_{i}^{N} S_i \rightarrow \min \]

where:

- \( N \) - number of the considered areas, where waste dumping is acceptable;
- \( i \) - the consecutive number of each considered area for waste dumping;
- \( C_{dis} \) - total costs for disturbing the initial terrain, acquired for waste dumping in area \( i \), USD (BGN);
- \( C_{tr} \) - total costs for overburden transportation to area \( i \), USD (BGN);
- \( C_{ci} \) - total costs for waste dump construction in area \( i \), USD (BGN);
- \( C_{rec} \) - total costs for waste dump area reclamation \( i \), USD (BGN);

\[ F_1 = \sum_{i}^{N} C_{dis} + C_{tr} + C_{ci} + C_{rec} = \]
\[ = \sum_{i=1}^{N} \sum_{j=1}^{n_i} \sum_{k=1}^{m_j} A_{ij} \sum_{k=1}^{m_j} \left[ \left( L_{ij} + \frac{K_{ij} H + (k - 1) H}{\sin \arctg i_{jk}} + L_{ij} \right) \gamma_o c_{tr} + c_c \right] \left[ K_{ijk} V_{ijk} + \sum_{k=0}^{k-1} K_{ij'k} V_{ij'} \right] \left[ c_{dis} + c_{rec} \right] X_{ijk} \]

where:

- \( n_i \) - number of alternatives for construction of the waste dump at location \( i \);
- \( j \) - serial number of the alternative to the construction of the dump;
- \( A_{ij} \) - Boolean variable, taking into account the choice of a single alternative \( j \) for location \( i \);
- \( m_j \) - number of dump benches for alternative \( j \);
- \( k \) - consecutive number of the dump benches for alternative \( j \);
- \( c_{dis} \) - relative costs for preparation of the area for the dumping of the dump, USD/m²;
- \( c_{tr} \) - relative costs for transposing the overburden, USD/(t.km);
- \( \gamma_o \) - bulk density of the overburden, t/m³;
- \( L_{ij} \) - transport distance to dump location with design alternative \( j \) for location \( i \), km;
- \( K_{ijk} \) - coefficient of proportionality of the volume dumped at bench number \( k \);
- \( H \) - height of the dump bench, m;
- \( i_{jk} \) - slope of the ramp connecting the dump benches, \( \% \);
- \( L_{ijk} \) - average transport distance for the \( k \)-th step of the \( j \)-th variant of the dump, located at location \( i \), km;
- \( c_c \) - relative costs for construction of the embankment, USD/m³;
- \( V_{sk} \) - volume of overburden in swollen state, necessary for construction of the \( k \)-th bench, m³;
- \( k \sum_{k'=0}^{k-1} V_{ijk'} \) - volume of overburden in the swollen state, necessary for the construction of the level \( k \)-1, m³;
- \( S_i \) - disturbed area, required for building the base of the waste dump in area \( i \), m².

Each considered area \( i \) can be used for developing \( n_i \) technologically feasible dump design alternatives, which are proven to pass a stability test (Hoek-Brown, Mohr-Coloumb, etc.)

The sum of the required areas for waste dumping can be calculated by the equation:

\[ F_2 = \sum_{i}^{N} S_i = \]
\[ = \sum_{i=1}^{N} \sum_{j=1}^{n_i} \sum_{k=1}^{m_j} \left[ K_{ij} V_{ijk} + \sum_{k=0}^{k-1} K_{ij'k} V_{ij'} \right] X_{ijk} \]

The sum of the preliminary operations for preparing the waste dump area, transportation costs for the overburden, operational costs for waste dumping and the reclamation costs can be calculated with the general formula:

\[ X_{ij} \] - Boolean variable, taking into account the level to which the dump is constructed;

\( K_{ijk} \) - factor taking into account the disturbing effect of the overburden from the \( k \)-th bench of alternative \( j \) for the dump, located at location \( i \), m³/m².

The \( K_{dis} \) factor takes into account the shape of the terrain on which the embankment is built. It is considered that a minimal negative impact on the environment is observed in case of violation of less amount of areas required for the waste dump construction. This factor is the reciprocal value of the capacity factor for the dumping area (Hristov and Aleksandrova, 2000). Therefore, the location of the dump is relative to the land shapes and the position of the dump will be more rational at minimum values of \( K_{dis} \), i.e. in negative land forms. Higher values for \( K_{dis} \) will be reached for dumping waste on steeper slopes.

In the case when the volume of overburden is dumped on previously disturbed areas during previous mining activities or on existing embankment benches for internal waste dumping, then \( K_{dis} = 0 \) m³/m², as no additional areas of the earth's surface are disturbed. By analogy with the method of prof. A.I. Aren'tiev (Anachkov and Konstantinov, 1985) for determining the integral schedule of mining works \( f(\Sigma P) = \Sigma V \), a similar function for the dumping works can be constructed, as in a coordinate system the volume of the overburden in swollen state for the dump building is compared with the area affected by it: \( f(\Sigma V) = \Sigma S \).

Where \( \Sigma P \), \( \Sigma V \) and \( \Sigma S \) is the general form for denoting the corresponding sums of volumes for ore, waste and required
dumping areas at reaching a certain stage of the mine’s life (on an annual base or at the point of reaching a new bench).

During the construction of the embankment facility, for each stage of dumping a given volume of overburden, it can be approximately established what area will be disturbed by it. Two curves can be compared on the integrated schedule, corresponding to two principally opposite options of the embankment construction: 1) for \( H \rightarrow \min \) (or \( B \rightarrow \max \)), 2) for \( H \rightarrow \max \) (or \( B \rightarrow \min \)), where \( B \) is the required width of the benches for waste dumping.

In the first alternative, the embankment is built bench by bench, thus it is necessary to disturb the maximum amount of areas for the construction of each subsequent level. In the second case, smaller areas of the terrain are disturbed, as the volumes of overburden are dumped in order for the waste dump to reach its maximum feasible height, while at the same time the benches have the minimum required width for placing the necessary machines. In Figure 1 a schematic diagram of the two curves of the two alternatives for dump building is represented.

This diagram could also be represented as a table for more tough cases of terrain, where the dependence is not as smooth. Nevertheless, it proves that the waste dump construction technology is a major factor for this dependence.

In order to obtain better accuracy for the required dumping area during the stages of dumping, the embankment bench can be divided into \( u \) segments by the number of segments forming the shape of the \( m \)-th bench for dump alternative \( j \). A necessary condition is that the segments should be linked to the technological sequence of the construction of the current embankment bench. Furthermore, each segment could be formed for reaching a certain height of the waste dump.

![Figure 1. Dependence between the disturbed area and the waste volume for waste dump building](image)

Nevertheless, the objective functions \( F_1 \) and \( F_2 \) acquire the form:

\[
F_1 = \sum_{i=1}^{N} \sum_{j=1}^{n_i} A_{ij} \sum_{k=1}^{m_j} \sum_{l=1}^{u_k} \left[ L_{ij} + \frac{K_{ijkl} \cdot h + (k-1) \cdot H}{\sin \arctg \frac{i}{p}} + L_{ijkl} \right] \cdot \gamma \cdot P_{cp} + P_{nu} \left[ K_{ijkl} \cdot V_{ijkl} + \sum_{k=0}^{k-1} V_{ijk} \right] + \left[ K_{ijkl} \cdot V_{ijkl} + \sum_{k=0}^{k-1} K_{ijkl} \cdot V_{ijk} \right] \cdot \left( c_{dis} + c_{rec} \right)
\]

\[
F_2 = \sum_{i} S_i = \sum_{i=1}^{N} \sum_{j=1}^{n_i} A_{ij} \sum_{k=1}^{m_j} \sum_{l=1}^{u_k} \left[ K_{ijkl} \cdot V_{ijkl} + \sum_{k=0}^{k-1} K_{ijkl} \cdot V_{ijk} \right] \cdot X_{ijkl}
\]

Whether solving the simpler version of the task or the option with the individual segments, it is necessary that the possible solutions meet each of the following limiting conditions:

1) \( \sum_{i=1}^{N} \sum_{j=1}^{n_i} A_{ij} = 1 \) \( A_{ij} = \{0; 1\} \)

2) \( \sum_{i=1}^{N} \sum_{j=1}^{n_i} A_{ij} \sum_{k=1}^{m_j} X_{ijk} = 1 \) \( X_{ijk} = \{0; 1\} \)

3) \( \sum_{i=1}^{N} \sum_{j=1}^{n_i} A_{ij} \sum_{k=1}^{m_j} \sum_{l=1}^{u_k} X_{ijkl} = 1 \) \( X_{ijkl} = \{0; 1\} \)

4) \( 0 \leq K_{ijk} \leq 1 \) \( (K_{ijk} \text{ is generated starting from } 0 \text{ and gradually reaches } 1 \text{ with a step for each alternative}) \)

Where \( V_o \) - volume of overburden, which is a subject to embankment, \( m^3 \);

\( K_{s} \) - swelling factor for the waste material (overburden).

For the calculation of the disturbed areas by means of the coefficients \( K_{dis} \) (or \( K_{dir} \)) the following alternatives exist:

- For the purpose of performing approximate calculations, it is assumed that the dependence \( f(\Sigma V) = \Sigma S \) is close to a linear one for each bench \( k \) (or each segment \( l \) for its corresponding bench \( k \), i.e. \( K_{dir} \) is linear for each interval \( k \) to \( k+1 \) (or \( l+1 \) for each \( k \)) and is determined by the equation:

\[
K_{dir} = \frac{S_{ij}}{V_{ijkl}}, m^2 / m^3 \text{ or } K_{dir} = \frac{S_{ij}}{V_{ijkl}}, m^2 / m^3
\]

- An interpolation polynomial \( P(\Sigma V) = \Sigma S \) with maximum degree \( k-1 \) (or \( k \) for each \( k \)) is used, as \( K_{dir} \) is determined by the equation:

\[
K_{dir} = \frac{P_{ij}}{V_{ijkl}}, m^2 / m^3 \text{ or } K_{dir} = \frac{P_{ij}}{V_{ijkl}}, m^2 / m^3
\]
The Boolean variables \( A_i \) and \( X_{ik} \) (or \( X_{ik} \)) express the branches in the decision tree on which the individual alternatives \( A_i \) and the possible end positions for the embankment are located. By means of the method of random search and the subsequent generation of numbers in the admissible intervals for \( A_i \), \( X_{ik} \) (or \( X_{ik} \)) and \( K_{ik} \) (or \( K_{ik} \)) a set of solutions \( W \) is formed, representing different distribution of the volume of overburden for the individual embankment sites and obtaining embankments with different construction.

Each of the dumping solutions (DS) can be represented as a point with coordinates \( DS_w (F_{1w}, F_{2w}) \), where \( w \) is the sequential number of the solution. The computer generated solutions and their respective points determine the boundary of the Pareto-optimal solutions, the values of which dominate over the rest of the generated solutions. The solution at a given point \( DS_w (F_{1w}, F_{2w}) \) is considered to dominate the solution \( DS_w' (F_{1w}', F_{2w}') \) when the implemented conditions are valid:

\[
F_{1w} < F_{1w}' \quad \text{and} \quad F_{2w} < F_{2w}'.
\]

Each of the points located on the Pareto boundary and each of the other points of the generated solutions are satisfying the system. From the obtained solutions at the Pareto boundary, depending on the difference in the disturbed areas between the solutions, the one that satisfies additionally introduced conditions, expressing the economic or environmental requirements, is selected.

**Example of the algorithm in practice**

A case study was made for a project for a metallic ore deposit. Two areas are taken into consideration and for each area two dump design alternatives are made. The bulk volume of waste for dumping is approximately 5 500 000 m³ (approximately 7 100 000 m³ after swelling).

Input data:
- \( N = 2 \) (feasible dumping areas);
- \( n_1 = 2 \) and \( n_2 = 2 \) (alternatives for each dumping area);
- \( L_1 = 1.1 \) km;
- \( L_2 = 1.7 \) km;
- \( \delta_i = 10\% \);
- \( y_0 = 2.1 \) t/m³;
- \( K_{ef} = 1.3 \);
- The step which changes the values for \( K_{ik} \) is 0.05.

**Dumping area 1, Alternative 1:**
- Average terrain slope: 12°
- Bench slope angle: 35°
- Bench height: 20 m
- Bench width: 15 m
- Number of benches: 3

**Dumping area 1, Alternative 1:**
- Average terrain slope: 12°
- Bench slope angle: 35°
- Bench height: 15 m
- Bench width: 10 m
- Number of benches: 4

**Dumping area 2, Alternative 1:**
- Average terrain slope: 7°
- Bench slope angle: 30°
- Bench height: 30 m
- Bench width: 15 m
- Number of benches: 1

**Dumping area 2, Alternative 1:**
- Average terrain slope: 7°
- Bench slope angle: 30°
- Bench height: 15 m
- Bench width: 10 m
- Number of benches: 2

For calculating \( K_{ij}^{dis} \), the linear alternative is chosen.

Table 1 represents the dependence between the dumped volumes and the disturbed areas:

<table>
<thead>
<tr>
<th>Area alternative</th>
<th>Design alternative</th>
<th>Bench number</th>
<th>Waste volume, m³</th>
<th>Total waste volume, m³</th>
<th>Disturbed area, m²</th>
<th>Total disturbed area, m²</th>
<th>Disturbance factor, m³/m²</th>
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<td>178070</td>
<td>246169</td>
<td>0.0090</td>
</tr>
</tbody>
</table>

Figure 2 represents the points of all the generated solutions, which fulfill the problem’s requirements.

**Figure 2. Dumping solutions for current case study**

The dominant solutions for this case study are shown as the circled ones. The mining engineer has the option to decide whether less disturbed area is preferable for the specific project, or it is preferable to have less total costs.

**Conclusions**

The optimality of the obtained solution depends on the following prerequisites:
- the number and accuracy of the available dump design surfaces;
- the choice of the method for calculating the \( K_{dis}^{ef} \) indicator;
- the size of the step through which the variable \( K_{ik} \) (or \( K_{ik} \)) takes values in the range \([0; 1]\);
- the type of the construction technology planned for building the waste dump (determines the segment design for each bench).
The advantages of the method include:
- The solution found provides an opportunity for rational use of the areas within the concession border for the implementation of the waste dumping activities;
- This method significantly reduces (but does not eliminate) the subjective factor in choosing the location of the embankment and the shape of its structure;
- The solution of the problem can be represented as an algorithm and solved repeatedly with the help of software;
- The method can be applied for selective waste dumping, which requires different sets of feasible dumping areas for each type of waste (overburden) or diluted ore with contents lower than the cut-off grade.
- The method can also be applied for optimising the costs and the required areas for building ore stockpiles, although certain changes in the costs sum have to be made.

Disadvantages of the method include:
- The solutions found are suboptimal, i.e. they are optimal for the set of solutions W (which is a subset of the set of all possible solutions) and do not always coincide with the optimal solutions for the global set of solutions;
- In order to obtain a more accurate and optimal solution, it is necessary to design more alternatives for the waste dumps, as well as to design more of their segments surfaces, representing the different stages of their construction.

Opportunities for improvement:
- For obtaining even better results and optimising the shape of the dumps (incl. transport costs and disturbed areas, also), the costs for technical and biological reclamation could be included in the target cost function, as well as the possibility for moving waste dumps in different time periods of the mine exploitation. In this way, the optimality of the solution is achieved in the long run until the final phase of the reclamation of the mine and its waste dump.

References
Aleksandrova, E., 1999. Algorithm for optimization of dump slopes in the East Maritza coal basin. – Annual of the University of Mining and Geology “St. Ivan Rilski”, XLII, 21 p. (in Bulgarian)
JET FANS EFFICIENCY IN TUNNEL EMERGENCY SITUATIONS

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ABSTRACT. Tunnel construction has become an important and growing activity. Tunnelling is an important part of transport infrastructure and is a part of the sustainable development of the country. The tunnel ventilation during construction and operation is part of the whole design procedure. Although ventilation might be performed with different approaches, longitudinal ventilation with jet fans is most often employed. The efficiency of such devices depends on several factors – design parameters, location in the tunnel, interaction with main current. The last one is crucial in emergency situations, especially during fires when both temperature and density of main current change. One important point in normal and emergency ventilation design is the downwind influence of jet fans. This paper presents a longitudinal scheme with jet fans. Based on energy and mass conservation, the interaction between the jet fan and the main current is considered, leading to expressions for areas of impact. Several models for fire temperature distribution downstream are presented, outcomes are compared and suggestions for use are made. Additionally, jet fan efficiency coefficients are adjusted due to modelling results.

Keywords: jet fans, longitudinal ventilation, jet fan efficiency, road tunnels

Introduction

Recently, road traffic has been increasing and, at the same time, requirements for quality of road conditions has also been increasing. Under such circumstances, it is worth constructing new tunnels as part of the infrastructure and rehabilitate existing ones. Bulgarian road facilities, being part of the trans-European system, have to comply with EU and national regulations (Naredba № RD-02-20-2). An important part of the said regulations concerns tunnel ventilation, the main goals being to extract exhaust products out of the tunnel, to maintain safe atmosphere inside the tunnel, and last but not least - to ensure safe evacuation and accident damage mitigation. Tunnels longer that 400 m should have mechanical ventilation, which may be achieved in different ways (Vlasseva, 2015) – longitudinal, transverse and semi-transverse. Longitudinal ventilation with jet fans is increasingly being employed nowadays for several reasons: reduced construction costs since there is no need for additional air inlet and outlet devices, no need for special infrastructure close to tunnel portals and special, costly, ventilation technique. At the same time, jet fan industry is successfully developing in terms of design, improved efficiency, sizing, and power. The required ventilation power at the design stage is part of the whole project. Different types of jet fans provide more possibilities for ventilation and choice of the most suitable devices for the given tunnel. Proper operation of installed power depends on several factors, some of which are discussed in this paper: interaction between jet fan and main current, influence of extreme conditions in the tunnel (such as fire), adjustment of rated efficiency of jet fans to real conditions. All of the above-mentioned makes tunnelling an important part of the traffic infrastructure of our country. Correct design and realisation reduce the construction and operational costs which significantly contributes to the sustainable development of the country.

Jet Fans’ Characteristics

Fig. 1 presents a typical jet fan design. The rotor is with symmetrical or asymmetrical blade profile. The models with symmetrical profile facilitate fan reversion, which makes them suitable for maintaining different current directions. The motors are 2 or 3-phase, reversible or non-reversible. The bearings are self-lubricating. The silencers are with double lining and the inner part is a perforated metal surface filled with noise-absorption material.

Mounting may be fixed or hinged depending on the installation place. Constructions with deflection blades at different angles and anticorrosion protection with galvanisation are available.

Fig. 1. Jet fan construction

Jet fans’ manufacturing characteristics include many parameters, which vary with producers. Some fan features, in relation to the problems discussed in this paper, include:

- Length, mm;
- Diameter (inner and outer), mm;
- Thrust, N;
- Power, kW;
- Velocity of outlet jet, m/s;
- Manufacturing effectiveness.

Jet fan producers offer a wide spectrum of dimensions and characteristics: wheel diameters from 350 to 1800 mm; power ratings from 13 to 100 kW; thrust range from 180 to 3000 N; velocity of outlet jet from 28 to 42 m/s. Effectiveness is approximately 0.87 – 0.85.

The jet kinetic energy of the fan transforms into kinetic energy of slow adjusting current, which causes the static pressure to rise. The jet expands, mixes with the main current, thus intensifying the tunnel flow. The distance downwind of the jet fan location, when this intensification takes place, is discussed below.
Theoretical Basis of Jet Fan Performance

In order to estimate the jet fan operation, air flows in a sector with jet fans are analysed. Fig. 2 shows the general layout of the section where:

- \( f_t, u_t \) - tunnel cross section [m²] and velocity [m/s] of main current;
- \( f_j, u_j \) - outlet cross section of jet fan [m²] and outlet jet velocity [m/s];
- \( L_1, L_2, L_{12} \) - distances ante- and post- jet fan location and total distance of the sector [m].

\[ \rho_j u_j^{-} = \rho_j u_j^+ (f_j^{-} - f_j^+), \quad u_t = \rho_j u_j^{-} - \rho_j u_j^+ (f_j^{-} - f_j^+) \]  \quad (3)

Adding the local losses of jet fan inlet / outlet and combining with expression (1) gives (Kempf, 1965):

\[ (P_2 - P_1) f_t = \rho_j u_j^2 f_t^+ + \frac{1}{2} \rho_j u_j^2 f_t^{-} - \frac{1}{2} \rho_j u_j^2 (f_j^{-} - f_j^+) u_j^2 \]  \quad (4)

where \( \bar{u}_j \) is the average velocity in the tunnel at a distance \( \Delta x \) downwind the fan.

According to the graph on Fig. 3, average velocity depends on jet expansion with distance. One approximation is given in Mutama (1995):

\[ \bar{u}_j = k \frac{D}{x} u_j \]  \quad (2)

where k is the mixing coefficient.

Fig. 2. Tunnel sector with a Jet fan

The real flow in a sector with jet fan is three dimensional. One two-dimensional top view is shown on Fig. 3. The distance in zone (IV) is where the jet from a fan loses its identity and mixes with the main tunnel flow.

Fig. 3. Velocity profile downwind the fan

One structural model is presented here (Kuda et al., 1999), based on:
- mass and energy conservation of both currents;
- jet fan energy conservation;
- pressure losses’ balance.

It is assumed that the air densities of main and secondary flows are nearly the same (\( \rho_j \approx \rho_t \)). Further, when there is a process which leads to a change in the density, it will be included in the analysis. Impulse conservation [N] is presented with the following expression:

\[ (P_2 - P_1) f_t = \rho_j u_j^2 f_t^+ - \rho_j u_j^2 f_t^{-} - \rho_j u_j^2 (f_j^{-} - f_j^+) u_j^2 + \frac{1}{2} \rho_j u_j^2 \Delta x \bar{u}_j^2 f_t \]  \quad (1)

where \( \bar{u}_i \) is the average velocity in the tunnel at a distance \( \Delta x \) downwind the fan.

According to the graph on Fig. 3, average velocity depends on jet expansion with distance. One approximation is given in Mutama (1995):

\[ \bar{u}_j = k \frac{D}{x} u_j \]  \quad (2)

where k is the mixing coefficient.

Fig. 4. Average velocity in the tunnel downwind the fan

Fig. 4 presents the average velocity, calculated by (2) with the following data: tunnel cross section \( f_t = 73 \text{m}^2 \); hydraulic diameter \( D_t = 7 \text{m} \); diameter and cross section of jet fan outlet \( d_j = 917 \text{mm}; f_j = 0.4 \text{m}^2 \). It is clearly seen that, at the distance of 35-40 m downwind the fan, the average velocity equals 2 m/s – velocity of the tunnel flow before the jet fan operation. The average velocity is one part of the problem. It is more important to include the pressure changes due to the jet fan operation, on the one side, and friction pressure losses, on the other. Mass conservation law (3) is applied and \( u_t \) (fig. 2) is expressed (formula 4):

\[ \rho_j u_j^{-} = \rho_j u_j^+ (f_j^{-} - f_j^+), \quad u_t = \rho_j u_j^{-} - \rho_j u_j^+ (f_j^{-} - f_j^+) \]  \quad (4)

Expression (5) takes into account all parameters of composite flows. The maximum pressure achieved by a jet fan is published in Beyer et al. (2016):

\[ \Delta P_{t, \text{theo}} = \rho_j u_j^2 f_t \left( 1 - \frac{u_j}{u_j^+} \right) \]  \quad (6)

Fig. 5 shows the difference between (5) and (6).

Fig. 5. Comparisson of maximum (6) and real (5) pressure
Further, the density of flow in the vicinity of fan operation should be defined. Air density depends on temperature. The temperature in the tunnel could change rapidly due to tunnel fire. The next part of the paper deals with the average temperature evaluation downwind the fire along the tunnel length.

**Temperature of fire gases of tunnel fire**

Different expressions for calculation of the average temperature of fire gases are published in specialised references (CETU, 2003; Lonermark, 2005; PIARC, 2007; DelRey, 2012). Some of them pay special attention to additional mass and composition of fire gases (Yotova et al., 2017). All expressions are based on energy conservation of mass flow, which gives the relation between the fire effective power and the flow parameters:

\[
Q_c = m c_p (T - T_o) = \rho u f c_p (T - T_o) W
\]  

(7)

where: \(Q_c = 2/3 Q_T [W]\) Part of HRR (Heat Release Rate) which is transferred by convection and radiation;

\(\dot{m} = \rho u f [kg] / s\) mass flow;

\(T, T_o [K]\) – fire source temperature and temperature before the fire starts.

Maximum temperature of fire source is obtained from (7):

\[
T_{max} = T_o + \frac{Q_c}{\rho u f c_p}
\]  

(8)

The average temperature downwind the fire depends on the heat losses due to convection and radiation. These heat flows are as follows:

Convection

\[
q_c = h_c (T - T_{wall}) \frac{W}{m^2}
\]  

(9)

Radiation

\[
q_r = \varepsilon \sigma (T^4 - T_o^4) = h_r (T^4 - T_o^4) \frac{W}{m^2}
\]  

(9a)

where: \(\varepsilon\) - wall emission capacity;

\(\sigma = 5.68*10^{-8} [W/(m^2*K)]\) - Stefan-Bolzmann constant

\(h_c, h_r [W/m^2K]\) - convective heat exchange coefficient.

The overall heat flow is the sum of (9) and (9a):

\[
q^* = h_c (T - T_{wall}) + h_r (T^4 - T_o^4) \left[ \frac{W}{m^2} \right]
\]  

(10)

In (CETU, 2003; PIARC, 2007) \(h_c\) is calculated by the expression (11):

\[
h_c = \frac{L}{8} c_p \rho u^* 1.07 + 12.7 (Pr^{0.8} - 1) \frac{L}{8}
\]  

(11)

where: \(L\) - dimensionless friction coefficients of tunnel walls,

\(c_p\) - specific heat capacity; \([J/kgK]\);

\(\rho\) - air density, \([kg/m^3]\);

\(u^*\) - air velocity at distance \(x\) downwind the fire \(u(x)\); \([m/s]\);

\(Pr\) – Prandl number.

Lonermark (2005) proposes an expression, where the distance \(x\) and Reynolds number take part:

\[
h_c = 0.026 Re^{-0.2} \left[ 1 + \left( \frac{D_o}{x} \right)^{0.7} \right] \rho c_p u^*
\]  

(12)

where: \(Re\) – Reynolds number;

\(D_o\) – hydraulic diameter; \([m]\);

After several calculations with the above expressions (9-12) some important clarifications are made:

- In (11) and (12) the velocity denoted as \(u^*\) should be recalculated for each distance downwind the fire, depending on the air density at this place \(u^* (x) = \frac{D_o}{\rho(x)} u_o\);

- In (11) the Prandl number (\(Pr\)) changes depending on the temperature (Fig. 6);

![Fig. 6. Pr number vs temperature](image)

![Fig. 7. Kinematic viscosity vs temperature](image)

The results obtained under (11) and (12) show small differences, but use of (12) is more appropriate for more accurate reflection of the convective heat transfer based on the Reynolds number, the hydraulic diameter \(D_o\), and the distance downwind the fire.

After the above clarifications, the heat balance equation is written (CETU, 2003; Lonermark, 2005; PIARC, 2007):

\[
-\frac{1}{4} D_o \rho c_p u^* \frac{dT}{dx} = h_c (T - T_o) + \varepsilon \sigma (T^4 - T_o^4)
\]  

(13)

From (13) \(\frac{dT}{dx}\) can be expressed:
\[ \frac{dT}{dx} = -\frac{h_f(T - T_o) + \varepsilon \sigma (T^4 - T_o^4)}{\frac{1}{4} D_H \rho c_p \mu^*} \]  \hspace{2cm} (14) \]

One iterative solution can be obtained by discretisation of the tunnel length in small steps \( \Delta x \) and the corresponding indexes:

\[ L_{\text{fire}} \leq x_i \leq L_{\text{tunnel}}; x_{i+1} = x_i + \Delta x \]  \hspace{2cm} (15) \]

Applying the above, the discretisation (14) can be written in the following way:

\[ \frac{dT_i}{dx_i} = -\frac{h_f(i-1)(T(x_{i-1}) - T_o) + \varepsilon \sigma (T^4(x_{i-1}) - T_o^4)}{\frac{1}{4} D_H \rho c_p \mu^*} \]  \hspace{2cm} (16) \]

Expression (16) gives the formula for temperature change evaluation in an interval \( \Delta x \). Then the value of the temperature in the next interval is calculated:

\[ T_{i+1} = T_i + \Delta T_{i+1} \]  \hspace{2cm} (17) \]

Another approximation of (13) is published in (DelRey, 2012; Beyer, 2012):

\[ T(x) = T_o + \left( T(x - \Delta x) - T_o \right) e^{-\frac{4 \Delta x}{\rho c_p \mu^*} \left( x - x_{\text{fire}} \right)} \]  \hspace{2cm} (18) \]

where: \( \phi_c, \phi_r \) are convective and radiative heat flows [W].

Fig. 8 shows comparison of results obtained by (16) and (18) with the same data: 100 MW HRR takes place on the 400 m of the tunnel portal in a 1200 m tunnel. The analysis of the results leads to the following conclusion: the temperature calculated with (18) reaches the initial one (290K) only 200 m downwind the fire. This result doesn’t correspond to real experiments, published by (Cafalo, 2010; Ingason, 2010), where fire influence is traced for longer distances, even to the other tunnel portal. That is why our recommendation is to use an iteration procedure (16), because at a project phase we should take into account a more realistic situation, rather than neglect the real danger. The required mechanical ventilation should be calculated based on accidental behaviour of the system.

\[ \eta = \left[ 0.0192 \left( \frac{z}{D} \right)^{-1} - 0.144 \frac{z}{D} + 1.27 \right]^{-1} \]  \hspace{2cm} (19) \]

Fig. 9 shows the velocity change downwind the fire by (16).
• velocity effectiveness $\eta_v$ – depends on the relationship between the main current and the outlet jet velocity;

$$\eta_v = 1 - \frac{u_j}{u_t}$$

(20)

• temperature effectiveness $\eta_T$ - depends on the flow density.

$$\eta_T = \frac{\rho_f}{1.2}$$

(21)

The jet fan performance reflects all four coefficients (22):

$$\eta_{eff} = \eta_{max} \times \eta_T \times \eta_v \times \eta_\rho$$

(22)

An overall expression for the performance evaluation taking into account the required number of jet fans ($n$), in combination with (5), (20), and (21) is presented below:

$$\eta = 100 \frac{\Delta P_{f} + (\zeta_0 + \lambda \frac{\Delta X}{D_f}) \frac{D_f}{2} u_t^2}{n \rho_f u_j^2 \left(1 - \frac{u_j}{u_t}\right) f_t f_j}$$

(23)

### Discussion

The impact of flow parameters in case of tunnel fire on the jet fan operation is shown in Table 1.

<table>
<thead>
<tr>
<th>Jet fan characteristics</th>
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<tbody>
<tr>
<td>Thrust $F_f$</td>
</tr>
<tr>
<td>Outlet velocity $u_f$</td>
</tr>
<tr>
<td>Diameter $D_f$</td>
</tr>
<tr>
<td>Distance to tunnel ceiling $z$</td>
</tr>
<tr>
<td>Manufacturing efficiency $\eta_{max}$</td>
</tr>
</tbody>
</table>

Table 1. Jet fan characteristics

Fig. 12 shows the velocity and temperature coefficients. It can be noticed that rapid decrease is observed in the vicinity of the fire source and 200 m downwind due to increase of the temperature and decrease of the density. Gradually, the coefficients become close to their initial values, but are not the same.

Fig. 13 shows the impact of fires with different HRR – 30, 50, 70 and 100 MW. Again, the biggest impact is 400 m downwind the fire. The conclusion is that, in these sectors, the jet fans will operate with lower effectiveness. In case of 30 MW HRR, the performance decreases by 14%, while for 100 MW fire this reduction is 40%. That means that our calculations based on the manufacturing effectiveness for the rated ventilation power should ensure reserves according to the methodology presented in this paper.

The obtained results once again confirm the rule for design of tunnel ventilation: it should be done based on design fires, located at different places inside the tunnel. Normal ventilation should use part of the overall capacity, enough to maintain the tunnel atmosphere within safety limits (Naredba Nr RD-02-20-2, 2015). Furthermore, the impact of the natural ventilation pressure on the mechanical ventilation should be analysed and taken into account in order to estimate fan reserves (Vlasseva and Dinchev, 2015).

### Conclusion

The results of this study can be summarised as follows:

• based on the mass and impulse conservation laws, expressions for interaction between the jet fan operation and the main tunnel flow are proposed;

• as a result of the thorough analysis of all available expressions for average tunnel fire gases’ temperatures and all influencing parameters, one iteration procedure is recommended. Its results are compared to real experiments;

• special attention is paid to the adjustment of fan performance in extreme conditions.

Future research might be targeted towards the work of paired jet fans (2 or 3 in parallel) (Guihong, 2014), the use of special directional blades at the inlet/outlet of the jet fan, and additional consideration of the mass generated by the fire source.

### References


Naredba № RD-02-20-2 ot 21 dekemvri 2015 g. za tehnicki pravila i normi za proektiranje na patni tuneli, DV broj 8, 29.01.2016.


PIARC, 2007. Systems and Equipment for Fire and Smoke Control in Road Tunnels, PIARC Committee on Road Tunnels (C5).


PROCESSING OF PYRITE CONCENTRATES WITH THE EXTRACTION OF NON-FERROUS METALS: NICKEL AND COBALT TECHNOLOGY ELABORATION

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ABSTRACT. The paper presents the results of the development of a technology for processing of pyrite concentrates with the extraction of non-ferrous metals, iron and sulphur using the technology of two-stage dissociating roasting with hydrometallurgical processing of cinder. Hydrometallurgical processing of cinder was studied. It comprised of two steps - cinder leaching and extraction for processing multi-component solutions. Based on the results of laboratory tests, balance experiments were conducted on the chemical enrichment of nickel-poor and cobalt-pyrite concentrates. The experiments included (i) Thermal decomposition of pyrite concentrate at a temperature of 660 - 700°C and a duration of 60 minutes, an oxygen flow rate of 30-50% of the stoichiometric; (ii) Leaching of the cinder with a HCl solution at a temperature of 90°C, liquid-solid = 8:1, pH 2.7 and a duration of 60 minutes; (iii) Filtration of pulp and precipitation of nickel and cobalt from solutions with iron sulphide. During leaching, mainly iron is transferred to the solution; nickel and cobalt remain in a small amount of cake (the cake weight is reduced by almost ten times compared to the thermal decomposition product). As a result, up to 99% of non-ferrous metals are extracted into the concentrate, and the solution becomes more concentrated in iron.

Keywords: pyrite concentrates, sulphidising roasting, nickel and cobalt, hydrometallurgical processing

Introduction

The processing of pyrite and pyrrhotite concentrates is carried out in Canada, Finland and Zambia. In Canada, oxidative roasting is used, followed by cinder processing to recover cobalt, nickel, and iron pellets. In Canada, the initial product is subjected to oxidative roasting, followed by processing of the cinder to recover cobalt, nickel and obtain iron-containing pellets (Morcali et al., 2017; Yang et al., 2019). In Finland and Zambia, the original concentrate is subjected to sulfatizing or dissociating roasting, followed by hydrometallurgical processing of the cinder. The residual concentration of cobalt in the waste cakes is over 0.4% in Zambia and about 0.2% in Finland (Günther, et al., 2012).

With an initial cobalt content of about 3% in Zambian concentrates and about 1.2% in pyrrhotite concentrates in Finland, the recovery of cobalt is 80–85%. The residual concentration of cobalt in dump cakes is over 0.4% in Zambia and about 0.2% in Finland (Günther, et al., 2012).

In general, the problem of processing stale tailings is a global problem, and the main task is to extract economically valuable metals: cobalt, nickel and copper (Wang et al., 2019), (Zhang et. al., 2013). Today more than 40% of cobalt is extracted from such raw materials. In Kazakhstan, the market for extracting cobalt from stale tailings is practically undeveloped. And the demand for nickel and cobalt is about 3–5 thousand tons per year.

World production of primary nickel in all forms in 2019, according to analysts at Wood Mackenzie, amounted to 2,235 thousand tonnes, including 1,153 thousand tonnes of nickel (51.5%) - in ferronickel and nickel iron alloys, the data are published by Li and co-authors (2015). The world production of refined cobalt, according to estimates by the Cobalt Institute (CI) - (formerly the Cobalt Development Institute), amounted to 124,3 thousand tonnes in 2019, which is 7,4 thousand tonnes more than in 2018 (Selivanov et al., 2019).

The main part of cobalt is used in the production of batteries (~76 thousand tonnes in 2019) and super-alloys (~17,6 thousand tonnes in 2019), and the level of production of rechargeable energy sources and, accordingly, the consumption of cobalt is growing steadily. So, if in 1995 the demand for cobalt in this consumption sector was estimated at 700 tonnes, then in 2014 it approached 40 thousand tonnes, and in 2019 - 76 thousand tonnes (60% of world demand). All other areas accounted for about 26% of global demand (Sadykov et al., 2020).

The Republic of Kazakhstan possesses huge amounts of raw materials, including nickel and cobalt ores. For example, the reserves of the Shevchenko deposit alone for nickel are 403,9 thousand tonnes, for cobalt – 23,4 thousand tonnes. The Gornostaevskoye deposit (Kazakhstan) contains 500 thousand tonnes of nickel reserves and 32,4 thousand tonnes of cobalt. Tailings from Sokolovsko-Sarbaiskoe mining and processing production association (Sokolovsko-Sarbaiskoe gornobogatitelnoe proizvodstvennoe obedinienie (SSGPO JSC)) represent technogenic raw materials containing more than 7 thousand tonnes of nickel and 14 thousand tonnes of cobalt per year. Despite the growing global trend in the consumption of nickel and cobalt in Kazakhstan, the extraction of these metals from domestic ores has not yet been organised. (Motovilov et al., 2018). The organisation of our own industrial production of nickel and cobalt from a significant amount of nickel- and cobalt-containing raw materials and man-made materials available in Kazakhstan is undoubtedly an urgent task.

At SSGPO JSC (Kazakhstan), in the course of many years of processing iron ores, a significant amount of tailings has accumulated, which are currently an additional potential source of raw materials. When processing sulphide-magnetite ores of the SSGPO JSC, waste is generated in the form of wet magnetic separation tailings, which in the amount of 8 million tonnes per year are stored in dumps. Tailings of wet magnetic separation (WMS) contain sulphur, cobalt, non-ferrous and precious metals, the production of which in annual terms can be approximately 400 thousand tonnes of sulphur (S), 400 thousand tonnes of iron (Fe), 1,2 thousand tonnes of cobalt (Co), 3 thousand tonnes copper (Cu), 0.5 thousand tonnes of...
nickel (Ni). At the moment, there are about 400 million tonnes of tailings suitable for processing. Precious metals are concentrated in old stale WMS tailings.

The research presented here is devoted to the development of a technology for processing pyrite concentrates with the extraction of non-ferrous metals, iron and sulphur using the technology of two-stage dissociating roasting with hydrometallurgical processing of cinder.

The aim of the work is to test the technology for processing old and fresh tailings of magnetic separation, to confirm the possibility of their economically feasible processing, to test the technology for processing pyrite concentrates, with the extraction of cobalt and nickel into commercial products.

**Thermodynamic research**

For the processing of Kazakhstani raw materials, the most acceptable is the use of combined technologies, including pyrometallurgical processing (smelting of oxidised or roasting of sulphide materials) with subsequent chemical enrichment of the products obtained by processes including acid leaching followed by precipitation from solutions of nickel and cobalt sulphides.

In order to find optimum treatment conditions thermodynamic calculations are needed. The results of thermodynamic studies of the selected processes are presented further.

**Thermodynamics of pyrometallurgical processes**

Chemical enrichment can be carried out by selective leaching or selective precipitation of metal compounds. The process can involve raw materials with preliminary pyrometallurgical preparation or without preparation. To substantiate the process of chemical enrichment, we have performed a thermodynamic analysis of systems including nickel, cobalt, iron, sulphur, oxygen under the conditions of pyro- and hydrometallurgical processing. The ways of sulphidising roasting were published earlier (Merkibaev et al., 2018).

Using the thermodynamic calculation programme HSC Chemistry 5 from Outokumpu, we calculated the thermodynamic characteristics of the main reactions and built isothermal sections of phase equilibrium diagrams in the systems Fe – O – S, Ni – O – S, Co – O – S at temperatures of 800–1100 K. It has been established that with an increase in the oxygen pressure in the system at a temperature of 900 K and a partial pressure of sulphur dioxide close to atmospheric \( \text{g}_{\text{S}} \text{O}_2 \approx 0 \) pyrite undergoes the following transformations - FeS\(_2\) → FeS\(_3\) → Fe\(_2\)O\(_4\) → Fe\(_3\)O\(_4\) → Fe\(_3\)O\(_6\) → Fe\(_3\)O\(_{12}\).

With a decrease in the concentration of \( \text{S}_2\), the transformation of iron disulphide takes place with the successive formation of lower iron sulphides: FeS\(_2\) → FeS\(_3\) → Fe\(_2\)S\(_3\) → Fe\(_3\)S\(_3\) → Fe\(_3\)O\(_6\) S → Fe\(_4\), these data are corresponding to (Bastow, et.al, 2018). Under the conditions of thermal treatment of pyrite in the presence of roasting gases, the aforementioned lower iron sulphides are formed, as well as Fe\(_3\)O\(_2\) and possibly FeS\(_2\).

For the thermodynamic analysis of the process of heat treatment of nickel-cobalt-containing sulphide raw materials, we have performed calculations of the Gibbs energy of the probable basic reactions (Table 1).

When roasting FeS\(_2\) in the presence of a limited amount of oxygen, iron sulphides of various compositions can be obtained by reactions (1-4): Fe\(_{0,877}\)S, FeS, Fe\(_{0,331}\)S, Fe\(_{0,33}\)S within the homogeneity region. In addition, according to reactions (4-9), depending on the roasting conditions, interconversions of the above iron sulphides can occur.

Nickel and cobalt sulphides behave in a similar way, so according to reactions 10 and 11, cobalt disulphide can pass into Co\(_{0,8}\)S\(_4\) and CoS, according to reactions 15, 16 - nickel disulphide passes into Ni\(_2\)S\(_4\) and Ni\(_3\)S\(_4\), according to reactions 12-14, 17-19, the transformation of cobalt and nickel sulphides occurs within the homogeneity region. With an excess of oxygen, oxygen-containing compounds of iron, nickel and cobalt are formed: metal oxides and sulphates.

Thus, based on the phase diagrams of Fe (Ni, Co) – S systems, it can be argued that, due to the presence of a wide homogeneity range, it is possible to ensure, under heat treatment conditions (700–1100 K), the formation of low-sulphur iron compounds of a wide range of compositions, as well as cobalt and nickel of variable composition, these are corresponding to (Zhang et al., 2019).

**Table 1. Thermodynamic analysis of possible reactions of dissociating roasting of materials**

<table>
<thead>
<tr>
<th>Chemical reaction</th>
<th>(\Delta G^0), kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1. \text{FeS}_2 + 1/2\text{O}_2 = 1/2\text{Fe}_2\text{S}_3 + \text{SO}_2)</td>
<td>-130,30 -143,19</td>
</tr>
<tr>
<td>(2. \text{FeS}_2 + 0,86\text{O}<em>2 = 1,14 \text{Fe}</em>{0,877}\text{S} + 0,86 \text{SO}_2)</td>
<td>-208,20 -245,42</td>
</tr>
<tr>
<td>(3. \text{FeS}_2 + \text{O}_2 = \text{FeS} + \text{SO}_2)</td>
<td>-241,97 -280,78</td>
</tr>
<tr>
<td>(4. \text{FeS}_2 + 6/7\text{O}_2 = 1/7\text{Fe}_2\text{S}_3 + 6/7\text{SO}_2)</td>
<td>-203,90 -237,17</td>
</tr>
<tr>
<td>(5. \text{FeS}_3 + 5/7\text{O}_2 = 2/7\text{Fe}_2\text{S}_3 + 5/7\text{SO}_2)</td>
<td>-147,20 -187,95</td>
</tr>
<tr>
<td>(6. \text{Fe}_2\text{S}_3 + 0,719\text{O}<em>2 = 2,281\text{Fe}</em>{0,877}\text{S} + 0,719 \text{SO}_2)</td>
<td>-155,60 -204,28</td>
</tr>
<tr>
<td>(7. \text{Fe}_2\text{S}_3 + \text{O}_2 = 2\text{FeS} + \text{SO}_2)</td>
<td>-223,34 -275,17</td>
</tr>
<tr>
<td>(8. \text{Fe}_3\text{S}_4 + \text{O}_2 = 7\text{FeS} + \text{SO}_2)</td>
<td>-266,49 -305,26</td>
</tr>
<tr>
<td>(9. \text{Fe}_{0,877}\text{S} + 0,123\text{O}_2 = 0,877\text{Fe}_2\text{S} + 0,123\text{SO}_2)</td>
<td>-29,66 -31,05</td>
</tr>
<tr>
<td>(10. \text{CoS}_2 + \text{O}_2 = \text{CoS} + \text{SO}_2)</td>
<td>-250,42 -268,37</td>
</tr>
<tr>
<td>(11. \text{CoS}_2 + 1,11\text{O}<em>2 = \text{CoS}</em>{0,89} + 1,11\text{SO}_2)</td>
<td>-279,36 -295,41</td>
</tr>
<tr>
<td>(12. \text{CoS}_{1,330} + 0,333\text{O}_2 = \text{CoS} + 0,333\text{SO}_2)</td>
<td>-80,14 -86,00</td>
</tr>
<tr>
<td>(13. \text{CoS}_{1,330} + 0,4,443\text{O}<em>2 = \text{CoS}</em>{0,95} + 0,4,443\text{SO}_2)</td>
<td>-109,07 -113,03</td>
</tr>
<tr>
<td>(14. \text{CoS} + 0,11\text{O}<em>2 = \text{CoS}</em>{0,93} + 0,11\text{SO}_2)</td>
<td>-28,94 -27,04</td>
</tr>
<tr>
<td>(15. \text{NiS}_2 + 2/3\text{O}_2 = 1/3\text{Ni}_3\text{S}_4 + 2/3\text{SO}_2)</td>
<td>-172,08 -183,36</td>
</tr>
<tr>
<td>(16. \text{NiS}_2 + 4/3\text{O}_2 = 1/3\text{Ni}_3\text{S}_2 + 4/3\text{SO}_2)</td>
<td>-344,68 -360,84</td>
</tr>
<tr>
<td>(17. \text{Ni}_3\text{S}_4 + \text{O}_2 = 3\text{NiS} + \text{SO}_2)</td>
<td>-263,38 -272,94</td>
</tr>
<tr>
<td>(18. \text{NiS}_2 + 2\text{O}_2 = \text{Ni}_3\text{S}_2 + 2\text{SO}_2)</td>
<td>-517,79 -532,46</td>
</tr>
<tr>
<td>(19. \text{NiS} + 1/3\text{O}_2 = 1/3\text{SO}_2 + \text{Ni}\text{S}_2)</td>
<td>-84,81 -86,50</td>
</tr>
</tbody>
</table>

**Thermodynamics of selective sulphide precipitation**

The values of the solubility products of iron, nickel and cobalt sulphides, the effect of acidity and oxidation potential of the system on the behaviour of sulphides during hydrometallurgical processes allow us to conclude that it is
possible to selectively dissolve iron sulphides from a mixture of nickel, cobalt and iron sulphides, and a possibility exists of selective precipitation of Ni and Co sulphides from ferrous solutions.

Based on the Pourbaix diagrams, it is possible to recommend carrying out the leaching process in the pH range of 0-2.5. In this case, nickel and cobalt can pass into the solution, which subsequently, in accordance with the values of the solubility product, can be precipitated in the form of sulphides, Figures 1 and 2.

![Fig. 1. "Potential - pH" diagram of the Ni-S-H₂O system](image1)

![Fig. 2. "Potential - pH" diagram of the Co-S-H₂O system](image2)

The study of the leaching process was carried out with a pyrite concentrate thermally decomposed at a temperature of 973 K for 30 minutes in glass flasks with a reflux condenser and a stirrer. The stirrer rotation speed in all experiments was kept constant. A sample weighing 10-20 grams was loaded into a flask and filled with a solvent. The flask was placed in a water thermostat, the temperature in which was maintained with an accuracy of ± 0.2°C. The duration of the experiments was counted from the moment the specified temperature was reached.

At the end of the experiment, the solid phase was separated from the liquid and washed with slightly acidified water. Then both phases were analysed for the content of iron, nickel and cobalt.

A preliminary study was made of the efficiency of using various leaching reagents at different amount, which were solutions of ferrous chloride, hydrochloric acid, sulphuric acid, and a mixture of hydrochloric acid with magnesium chloride. Comparison of various reagents showed that the greatest extraction of cobalt and iron into solution is achieved when a mixture of hydrochloric acid and magnesium chloride is used as a solvent.

The concentration of hydrochloric acid used for dissolution was taken on the basis of operating conditions in a closed cycle with the possibility of solvent regeneration, as well as obtaining the smallest volumes of solutions. With the hydrothermal decomposition of chloride salts, hydrochloric acid with a concentration in the range of 250 g/L HCL can be obtained. This concentration of acid provides the receipt of rich solutions close to saturation in iron.

In the second series of experiments, the effect of temperature on the leaching process was studied. The amount of solvent was taken 1,04 times the theoretically required, the leaching time was taken equal to 2 hours.

**Flotation experiments**

Laboratory flotation studies were carried out on standard laboratory flotation machines with chamber volumes of 3, 1.5, 1, 0.5, and 0.25 litres. When performing studies on flotation, the following reagents were used: butyl xanthate - collector (activity 84.5%); T-80 – foaming agent (100% activity); flotation was carried out with tap water at pH – 7.7.5. Experimental work was carried out in a closed cycle (7 samples).

**Thermal decomposition of pyrite concentrate**

Thermal decomposition was carried out in a fixed-bed reactor, a sample was placed in a quartz tube, closed on both sides with plugs, and the temperature was automatically maintained at a given accuracy. The resulting product was analysed by the X-ray phase method for composition.

**Leaching of thermally decomposed pyrite concentrate**

The objectives of this study are to establish the optimal conditions for the selective and combined extraction of cobalt and nickel by extraction with an extractant CYANEX 272, re-extraction of metals from solutions of complex composition, as well as the conditions for the extraction of impurities of iron and cobalt from solutions.

We used the obtained solutions after one-stage leaching of thermally decomposed pyrite-cobalt concentrate, containing about 190 g/L of iron and about 500 mg/L of nickel and cobalt. Also, as comparative experiments, the salts CoSO₄•7H₂O and

**Materials and methods**

**Materials**

In order to use the tailings accumulated at SSGPO JSC as an additional potential source of raw materials, it became necessary to conduct research to develop a technology for their processing using flotation and magnetic separation processes.

We received two samples for the study, represented by old stale and current tailings of WMS of SSGPO JSC. The mass of the sample of current tailings was 500 kg with a maximum size of individual grains 3-4 mm. The sample weight of old stale tailings was 540 kg with the maximum size of individual grains up to 5 mm.

The chemical composition of the original current WMS tailings was, in %: Fe₂O₃ – 12.62; Cu – 0.05; Co – 0.013; Ni – 0.0081; S₂O₃ – 3.46; Pb – 0.019; Zn – 0.069; SiO₂ – 40.23; Al₂O₃ – 18.97; CaO – 12.59; MgO – 4.72; TiO₂ – 0.59; As – 0.006 and other elements.
NiSO₄·7H₂O were used to prepare synthetic solutions. The required pH value was maintained for 5-90 min, then the pH value changed slightly.

The extraction was carried out on an EL-1 laboratory extractor with stirring and regulation of the pH of the solution. The pH of the medium was adjusted using NaOH and H₂SO₄ solutions. The experiments were carried out at room temperature. The extraction results were evaluated by the residual concentration C (in g/L) of metal ions in the raffinate, the distribution coefficient D = C_{org}/C_{aq}, the extraction of metals into the organic phase, the separation coefficient β = D_{max}/D_{max}.

Re-extraction of metals from the organic phase was carried out with sulphuric acid solution with a concentration of 100–200 g/L.

**Hydrothermal decomposition of ferrous chloride**

The optimal decision for the processing of chloride solutions for marketable products obtaining is the hydrothermal decomposition, high-temperature hydrolysis. As a result of precipitation from solutions of nickel and cobalt sulphides, the solution contains, in g/L: Fe - 185 – 195; Ni 0,01 – 0,04; Co 0,005 – 0,01.

The reaction taken as the basis in experiments on high-temperature hydrolysis of FeCl₂·4H₂O crystals is:

5FeCl₂·4H₂O + O₂ = Fe₂O₃ + Fe₃O₄ + 10HCl + 15H₂O.

For the regeneration of hydrochloric acid, the solutions of ferrous chloride were subjected to hydrothermal decomposition. In general, the temperature conditions for the hydrothermal decomposition of ferrous chloride were studied.

The scheme for studying hydrothermal decomposition is presented in Fig.3.

The calculation of the degree of decomposition was determined by using the amount of hydrochloric acid formed in the temperature range 603-903 K (decomposition of FeCl₂·4H₂O), 453-503 K (decomposition of FeCl₂·6H₂O) and duration up to 180 minutes.

In the first series of experiments, the effect of the amount of solvent on concentrate leaching was studied, and the possibility of selective leaching was tested. As can be seen from the data, there is no selection at the boiling point of the solution and lack of acid. There is only some difference in the degree of decomposition of compounds of nickel, cobalt and iron.

**Results of leaching of thermally decomposed pyrite concentrate**

The results of leaching the thermally decomposed pyrite concentrate with acid solutions with a concentration of 0,5N are shown in Table 3 and Fig.4.

In the first series of experiments, the effect of the amount of solvent on concentrate leaching was studied, and the possibility of selective leaching was tested. As can be seen from the data, there is no selection at the boiling point of the solution and lack of acid. There is only some difference in the degree of decomposition of compounds of nickel, cobalt and iron.

<table>
<thead>
<tr>
<th>T, K</th>
<th>The amount of acid, a multiple of stoichiometric, R</th>
<th>Fe</th>
<th>Ni</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>379</td>
<td>0,52</td>
<td>120</td>
<td>69,11</td>
<td>60,58</td>
</tr>
<tr>
<td>379</td>
<td>1,95</td>
<td>120</td>
<td>97,85</td>
<td>100,0</td>
</tr>
<tr>
<td><strong>Decomposition with hydrochloric acid</strong></td>
<td><strong>Influence of the amount of solvent</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>379</td>
<td>20</td>
<td>1,04</td>
<td>61,98</td>
<td>45,15</td>
</tr>
<tr>
<td>379</td>
<td>20</td>
<td>1,04</td>
<td>79,03</td>
<td>95,18</td>
</tr>
<tr>
<td>379</td>
<td>20</td>
<td>1,04</td>
<td>97,43</td>
<td>95,81</td>
</tr>
<tr>
<td>379</td>
<td>379</td>
<td>1,04</td>
<td>3,5</td>
<td>83,50</td>
</tr>
<tr>
<td>379</td>
<td>379</td>
<td>1,04</td>
<td>240</td>
<td>97,43</td>
</tr>
<tr>
<td><strong>Decomposition with sulphuric acid</strong></td>
<td><strong>Influence of the amount of solvent</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>379</td>
<td>20</td>
<td>1,04</td>
<td>379</td>
<td>59,91</td>
</tr>
<tr>
<td>379</td>
<td>379</td>
<td>1,04</td>
<td>120</td>
<td>95,03</td>
</tr>
<tr>
<td>379</td>
<td>379</td>
<td>1,04</td>
<td>240</td>
<td>95,43</td>
</tr>
</tbody>
</table>

With an excess of solvent over 4% of the theoretically required amount, the thermally decomposed pyrite concentrate is almost completely leached, and an increase in the amount of solvent mainly affects the recovery of nickel. Thus, leaching of a thermally decomposed concentrate does not require large excess of solvent, all the more so if one performs...

Fig. 3. Installation diagram for hydrothermal decomposition of ferrous chloride

**Results and discussion**

**Flotation experiments**

The results of the flotation experiments are presented in Table 2.
countercurrent continuous leaching rather than periodic one-stage leaching.

The research results from studies on the temperature effect on leaching are shown in Fig. 4. From the results obtained it follows that the thermally decomposed concentrate is leached relatively easily. The most complete dissolution of the components of the concentrate is achieved at the boiling point of the solutions - at 379 K. There is some difference in the leaching rates of nickel, cobalt and iron. Nickel is leached most slowly. The optimum temperature range for leaching is 353 – 379 K.

Thus, on the basis of the studies carried out, the conditions for carrying out one-stage leaching of thermally decomposed pyrite-cobalt concentrate were determined - temperature 80 – 379 K; duration 2-4 hours, excess solvent 4-5%. Residual acidity under these conditions is 6-8 g/L, the solid yield is 7-9% of the original.

The solutions after leaching contain about 190 g/L of iron and about 500 mg/L of nickel and cobalt.

Under these conditions, the extraction into solution is:
- cobalt – 92.04–96.54%;
- iron – 94.03–97.4%;
- nickel – 95.18–95.81%.

The pulp after leaching settles well, filtration proceeds at a high speed.

**Approbation of extraction technology for the separation of elements, including the processes of refining and concentration of productive solutions**

Based on the results of experiments on metal extraction at various pH values of the solution, the dependence of the distribution coefficients of metals on pH (Fig. 5) from individual solutions of salts and from solutions of a mixture of CoSO₄ and NiSO₄ was plotted.

![Fig. 5. Dependence of the separation coefficient of metals (βCoNi) on the pH of the solution](image)

The obtained experimental data indicate that the CYANEX 272 extractant extracts cobalt and nickel ions quite well. The degree of extraction of cobalt from the leach solution reaches 99% at pH 6.5; the degree of extraction of nickel is 98% at pH 8-8.5. The calculated values of the metal separation coefficient indicate that the optimal pH of the medium for the separation of these metals is pH 5.5, where the metal separation coefficient reaches its maximum value and is 614. An increase in the solution pH leads to an increase in nickel co-extraction.

The re-extraction (with a sulphuric acid solution with a concentration of 160 g/L) was 97% for cobalt and 95% for nickel. As a result, a solution of the composition, mg/L: 470 Co, 23.75 Ni was obtained. Composition of raffinate was, in mg/L: 15 Co, 475 Ni.

**Selection of technology for chloride solutions processing**

At process temperatures below 603 K, the decomposition of FeCl₂•4H₂O practically does not occur, and FeCl₂•6H₂O decomposes noticeably at temperatures above 453 K.

The oxidised iron powders obtained as a result of hydrolysis were subjected to a comprehensive certification of their properties.

The end products of high-temperature hydrolysis of FeCl₂•4H₂O crystals with incomplete decomposition (no more than 60%) is magnetite, and with more complete decomposition, a mixture of magnetite and hematite powders.

Thus, technological scheme for processing ferrous chloride solutions has been elaborated, which includes: purification of ferrous chloride solutions from impurities; separation of crystals FeCl₂•4H₂O - saturation of the initial solution by evaporating it to 40% by volume, cooling and crystallisation at a temperature of 298 K; - dehydration of FeCl₂•4H₂O crystals by centrifugation; high-temperature hydrolysis of FeCl₂•4H₂O crystals at 873 K in a fluidized bed furnace; purification of a steam-dust-gas mixture in a cascade of precipitation cyclones; condensation of the vapour-gas mixture to obtain a circulating hydrochloric acid solution.
As a result, an ultrafine powder was obtained using the technology of high-temperature hydrolysis of FeCl₂·4H₂O at 903 K, the particles have a spherical and rhombic shape, and also have a high magnetic susceptibility.

**Conclusion**

A technology is developed for processing pyrite concentrates with the extraction of nickel and cobalt, iron and sulphur using dissociating roasting followed by hydrometallurgical processing of cinders. The testing of the extraction technology for the separation of elements, including the processes of refining and concentration of productive solutions, with the extraction of cobalt from the leaching solution up to 99% and the degree of nickel extraction up to 98%, has been carried out.

As a result of processing of ferrous chloride solutions to obtain ultra-dispersed powders of iron oxides by high-temperature hydrolysis, the corresponding technology was elaborated.

For the chemical enrichment of pyrite nickel-containing concentrates the technological flowsheet, presented in Fig. 6, is proposed. The proposed technology makes it possible to obtain rich iron-containing solutions that can be processed to obtain iron and its compounds.

![Fig. 6. Technological flowsheet of chemical enrichment of pyrite nickel-containing concentrates](image-url)
STUDY OF THE RELATIVE ENERGY CONSUMPTION OF A DRUM MILL TYPE
SAG 8.5 X 5.3

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2 University of Mining and Geology “St. Ivan Rilski”, 1700 Sofia, petko.nedyalkov@mgu.bg
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ABSTRACT. The article discusses the topic of the specific power consumption of a drum mill type SAG 8.5x5.3. The purpose of the study is to determine the influence of some basic parameters like angular velocity of the mill drum, the wear on the drum’s lining, mass of the mill filling, loading rate of the mill with ore and flow rate of incoming water of the product to be milled on the relative power consumption of the mill for maintaining quality. To determine the energy consumption of the mill, the listed parameters were measured and a Fisher matrix was constructed. In accordance with the selected target function, energy consumption patterns are synthesised depending on the loading rate of the mill with ore, the mass of the mill filling, the flow rate of the incoming water and the wear on the drum’s lining. Data processing was performed using the STATGRAPHICS computer programme and an adequate model has been found according to the selected target function. The target function has been found to satisfy the conditions for maintaining quality and reducing costs.

Keywords: drum mill, relative power consumption, mass of the mill filling, loading rate

Introduction

One of the main goals in modern production is to reduce harmful emissions, reduce production costs, and improve quality of production or energy use (Utu et al., 2018; Nyandwe et al., 2020). It is not always possible to achieve these goals simultaneously. Given the high cost of electricity and the generated harmful emissions during its production, it is appropriate for the main target function in energy-intensive industries to reduce energy consumption while maintaining the quality of production. Such industries are the crushing and milling of ore in the mining industry. It is known that the high quality of the product of these two processes leads to lower prices and higher product quality in the next process - flotation (Boteva et al., 2003). Therefore, the purpose of the present study is to determine a minimum power consumption model for a SAG 8.5x5.3 drum mill.

Choice of control parameters and target function

Clearly formulating the purpose of the study is a fundamental and important step in determining the target function. A poorly worded goal leads to inefficient control of the object. Of course, when the goal changes, the target function must change, and hence the research.

The choice of a target function is the most important task in modelling objects, and it is allowed to apply the methods of mathematical statistics. In this case, the object is a mill. This is a multifactorial object with nonlinear influence of the parameters relative to each other.

The first task in the modelling of drum semi-autogenous mills (SAG Mills) is the clear formulation of the goal. Given the weak data on the subject of the study and the high complexity of the object (mill), it is clear that this step is one of the most difficult and at the same time one of the most responsible. The aim, when formulated incorrectly, makes the research meaningless or at least incomplete. Obviously, in order to achieve this goal, first of all, it is necessary to characterise it clearly and strictly.

The choice of a target function, allowing the application of the methods of mathematical statistics is a step in the process of modelling (Bojanov et al., 1973; Bojanov et al., 1979). For this reason, the target function is formulated according to some certain requirements.

A properly formulated target function is characterised by quantity, i.e. each combination of values of the input factors to be characterised by a number. The set of values that the target function can accept is called the domain of its definition. This area can be definite or indefinite, continuous or discrete. The target function needs to be measurable in order to be set. The target function must be unitary.

In many cases, this requirement is met automatically because the goal is set strictly and its characteristic is one. The most common functions of this type are economic goals (costs, energy consumption, etc.) (Nikolov and Nikolova, 2006).

The target function must be effective, i.e. to effectively characterise the work of SAG Mills in accordance with the set goal. In addition, the efficiency of the target function does not remain constant in the process of research and optimisation. For example, when organising production in the initial stage, the most effective target function is the volume of production. When the final opportunities for increasing production are reached, the role of other parameters such as quality, production cost, etc. acquire significance. Therefore, once the target function is selected, it will not be considered an invariant parameter. At some point in the study, it may need to be replaced with another, more effective, target function.

The requirement for efficiency is also directly related to the requirement for completeness of the target function. This means that the target function must characterise extensively and fully the desired objective. The target function must also be statistically effective, i.e. with the minimum possible variance 2. In practice, this requirement is limited to the choice of a target function that can be measured (calculated with the greatest possible accuracy).

In the present study, the energy efficiency per unit of product - E, kWh/t - the amount of electricity consumption per unit of production was chosen as a target function (Hristova et al., 2018; Istalianov and Lakov, 2019).

Of course, other target functions can be accepted, such as the wear of the drum linings per tonne of milled product with
parameters such as change in the trajectory of the particles (Stoyanov, 2015), humidity, hardness and others. These target functions may be more noticeable after describing the most significant and specific phenomena in the process of milling materials in SAG mills.

It can be said that the chosen target function meets the condition of efficiency, has a clear physical meaning and has a quantitative characteristic - for each set of values of its factors an exact number of its defining region can be assigned. As a starting parameter, energy consumption is also statistically efficient, as the value can be accurately measured.

Energy consumption is a parameter that characterises the process in quantitative terms and this determines its main disadvantage - it is not the only one (Nikolova and Nikolov, 2006). Results from the experiment

In a previous study (Hristova, 2015) the independent influence of factors such as the amount of the processed ore, the mill speed, the filling with water and ore on energy consumption was analysed. The parameters - the quantity of ore and water are basic for the quality of the milled product in the semi-autogenous mills and for this reason their joint influence on the relative specific consumption of electricity has been studied. To obtain a real picture of energy consumption as a target function, it is necessary to include more input parameters - motor power P, kW; motor speed n, min⁻¹; amount of water Qw, m³/h; amount of ore Q, t; mass of filling M, t; yield of the estimated class of the final product K, %.

The specified parameters were measured during the operation of a real object drum mill type SAG 8.5x5.3. The values of the measured parameters are given in Table 1.

Table 1. Table with data for measured parameters

<table>
<thead>
<tr>
<th>№</th>
<th>Processing</th>
<th>P</th>
<th>n</th>
<th>Qw</th>
<th>Q</th>
<th>M</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>552855</td>
<td>1062,6</td>
<td>14,3</td>
<td>233</td>
<td>107,3</td>
<td>81,43</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>654145</td>
<td>1067,2</td>
<td>19,86</td>
<td>135</td>
<td>103,5</td>
<td>75,7</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>744820</td>
<td>1087,6</td>
<td>44,86</td>
<td>258,4</td>
<td>99,33</td>
<td>78,66</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>849393</td>
<td>1092,3</td>
<td>35,85</td>
<td>189,97</td>
<td>93,3</td>
<td>80,42</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2400</td>
<td>1060,2</td>
<td>25,25</td>
<td>238,4</td>
<td>110,5</td>
<td>74,96</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>98219</td>
<td>1004,3</td>
<td>29,53</td>
<td>207,3</td>
<td>114,2</td>
<td>78,34</td>
<td></td>
</tr>
<tr>
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Statistical survey of the results of the passive experiment of a drum mill type SAG 8.5 x 5.3

The investigated target function is the relative energy consumption E, kWh/t, which is a result of the ratio of the power of the mill motor measured by the sensors and the productivity of the mill for the final product per unit time.

The relative energy consumption is obtained by the formula:

\[ E = \frac{P}{Q}kWh/t, \]  

where:

- \( P, kW \) - the power, consumed by the drum motor;
- \( Q, t/h \) - the productivity of the mill.

The relative productivity of the mill is calculated according to the following formula:

\[ Q_1 = \frac{Q}{K}, t/h, \] 

where:

- \( Q, t/h \) - in practice is the loading rate of the mill with ore.
- \( K, \% \) - the yield of the estimated class of the final product, - the ratio of the class - 0.08 to the total quantity processed by the mill drum. It is obtained after a sieve analysis of the obtained material at the outlet of the mill.

The measurement results obtained are given in Table 2. In this table the treatment of the mill (from the moment of laying new drum linings to the moment of measurement) is represented by the percentage of the wear of the lining.

In this situation 0% corresponds to a new lining and 100% to a completely worn lining.

The data processing in Table 2 is performed by statistical analysis. The whole matrix for the relative energy consumption is processed.

Various methods, algorithms, mathematical apparatus (Mryankov, 2007), machine algorithm for calculation, neural networks are used to achieve the optimal parameters of the surveyed objects. In this case the results of the experiment is appropriate to be statistically processed using the STATGRAPHICS programme. The results of the statistical analysis of the relative energy consumption are shown in Table 3.

The evaluation of the significance of the regression coefficients is performed according to the Student's criterion (t-criterion) at a significance level \( \alpha = 0.05 \) and at least 8 degrees of freedom (DF). The programme evaluates the probability of significance of the regression coefficients, i.e. whether they fall within the confidence interval. If this probability is:

\[ P - Value < \alpha, \]  

so the coefficient of regression is significant (\( \alpha - \) confidence probability).

Similarly, the adequacy of the equation is assessed by the significance of the Fisher test (F-Ratio).

For the practical purposes of the study operational process, models and regressions are sought, which can be assumed with probability levels of 95% and it is expected that acceptable engineering errors of 5% will be acceptable for technical devices, such as drum-autogenic mills - type SAG 8.5x6.3.

Given the parameters of this model (Table 3), it is obvious that the multiple correlation coefficient \( R^2 \) is 98.28% and the corrected multiple correlation coefficient \( R^2 (adj) \) is over 98%.

The value of the reliability probability indicator (P-criterion) for the model is below the critical one, i.e. it can be assumed that the model is adequate. The degrees of freedom are 35 and are well above the required 8.

Therefore, the equation of the model describing the relative energy consumption with the natural variables will be:

\[ E = 73,753.10^{-3}. i - 87,6392.10^{-3}. Q + 0,327158.10^{-3}. n. M, kWh/t \]  

The correspondence between the model values and the experimental data is shown in the comparative diagram in Figure 1.

In the present study, when processing the data, the parameter amount of water \( Q_w, t/h \) did not correlate with the other parameters and therefore it is not included in the model.

### Table 2. Achieved measurement results

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### Table 3. Parameters of the most adequate model

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$R^2 = 0$  

$R^2$ (adjusted for d.f.) = 98.1751%  

Standard Error of Est. = 2.29509  

Mean absolute error = 1.61305  

Durbin-Watson statistic = 1.44291  

Lag 1 residual autocorrelation = 0.272021
Conclusions from the obtained experimental results

The results of the measurements and the statistical analysis of relative energy consumption show the following:

- the relative energy consumption is influenced to the greatest extent by four parameters, namely: the wear of the drum lining, the speed of the drum of the mill, the filling mass and the rate of loading of the ore into the mill;
- this study did not confirm the effect of the amount of water on energy consumption. The reason is the complex influence of a large number of other factors;
- with the increase of the wear of the milling drum lining increases the relative energy consumption of the mill, most likely due to the fact that the larger drum volume increases the relative speed of the drum. This increases the power to raise balls and large pieces of ore;
- the increase in drum speed also leads to an increase in power consumption - a well-known law of physics which confirms the result of the previous study;
- the rate of loading of the ore increases with the relative energy consumption decrease, which is probably due to the fact that the mass of the ore does not affect the power of the mill on the one hand, and on the other - the addition of more ore also leads to more final product (higher relative productivity);
- as the mill filling increases, the relative energy consumption of the mill also increases because most of the energy is drawn to lift balls and large pieces of ore. This is an obvious conclusion, the mention of which is incorrect to omit.

The team believes that such a study should be repeated as the low energy consumption parameters are taken after the study of the relative indicators of the finished product and the study of the yield of the evaluated class. In this case, a comparison can be made by simultaneously achieving two or three target functions - high product quality and low energy consumption.

References


Stoyanov, A., 2015. A task for the movement of a rigid body with the fixed point. Annual of the University of Mining and Geology “St. Ivan Rilski”, 58, (3), 119–121. (in Bulgarian with English abstract)

CONTROL OF BLAST-INDUCED SEISMIC ACTION GENERATED BY TECHNOLOGICAL BLASTINGS

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ABSTRACT. This article presents some of the studies on drilling and blasting technologies applied in the Assarel copper mine. The main emphasis is on examining the seismic effects on a particular engineering facility, located on the territory of the mine - CPT-3. The assessment of the blast-induced seismic loading on the structure is based on an analysis of the registered data on the site. Recommendations for the design of blasting parameters are provided.

Keywords: blast-seismic impact, drilling and blasting technologies, blast-induced seismic vibrations, technological blasting

Introduction

The side effects of the explosion are the subject of in-depth theoretical and experimental research. The management of the side effects is especially relevant for open pit mines. The main goal is complete safety for the environment due to:

- the complex (unique) mining and geological conditions of the deposits;
- continuous implementation of new, up-to-date and high-performance extraction technologies, depending on the construction of unique mining facilities;
- the tendency to apply restrictions on the permissible effects on the human body and protected sites in recent years in the world explosive practice (Mitkov, 2010a).

The impact, induced by technological blasts should be predicted, studied and controlled by the blasting engineer as part of the organisation of the working process. The proper implementation of this activity is critical for the technical and economic efficiency of the drilling and blasting (D&B) operations (Mitkov, 2007).

Hence it follows the main goal of technological blasting, exactly the optimisation of the parameters of blasting operations to achieve maximum blasting effect, defined in the mining practice worldwide:

- complete removal of the rock massif within the design contour of the blast field with conditioned grain size distribution of the destroyed material;
- guaranteed protection of the environment from the undesirable (and in some cases harmful) effects of the explosion, to a level that is practically completely safe.

The concept of "side effects" of the explosion, the parameters of which must be managed to a level completely safe for the environment is correctly defined as blast-induced seismic, air-blast, fly-rocks, toxic fumes, released during explosive decomposition (Mitkov, 2014b, Shishkov et al., 2019).

The defined term "criterion" expresses the maximum permissible limit values of the side effect, in the display of which its level is still within the safe limits, i.e. where no damages are inflicted on the protected sites (Mitkov, 2009).

The safe limit value for the effects of blast-induced seismic action on the environment is formulated as:

- limitation of relative deformation in the rock massif in the area: outside the borders of the blasting field, respectively in the area of the foundation of the protected structures - buildings, facilities, causing the initiation of plastic deformations;
- restriction of the development of the existing defects and appearance of new ones in the construction of the built structures;
- prevention of its impact on workers in the protected sites, causing mental stress;
- reduction of the risk of damage to highly sensitive equipment located in the protected sites (computers, relay stations, electronic microscopes, etc.).

The accepted criteria for blast-induced seismic effect are the criteria generally accepted in the international blasting practice:

- for protection of the rock massif - Coefficient of residual deformations (ε = PPV / C);
- for protection of constructed structures - Velocity of blast-induced seismic vibrations - PPV, mm/s;
- for impact on workers - PPV mm/s.

The permissible vibration velocity in accordance with the accepted criteria is the maximum value of blast-induced seismic vibrations (PPVz, mm/s), shown in the foundations of the protected object - foundation or rock massif, which guarantees prevention of residual deformations in the rock medium, respectively:

- creating conditions for the development of the existing defects (cracks) and the appearance of new ones in the construction (plaster) of the building;
- development of new micro and macro disorders (Mitkov, 2014a).

In accordance with the requirements of the Bulgarian local legislation (Ordinance № RD-02-20-2 for design of buildings and facilities in earthquake areas in force as of 15.03.2012), the determined Guidelines on blast-induced vibrations are adjusted to the seismic coefficient - design ground acceleration (Kc = 0.27) concerning the protection of buildings and facilities (Mitkov, 2015).

Research methodology

The detailed studies were performed in a real rock massif with modern specialised equipment:

- earthquake registration equipment, completed according to the methodology of the Geophysical Institute of the Bulgarian Academy of Sciences (1964 - 1994);
- UVS 1608 - chronological recording device, 8-channel version DIN, Nitro Consult AD, Stockholm - Sweden (1994 - 2008);
Studies to establish the generation and distribution of the blast-induced seismic impact on the environment have been carried out in accordance with the developed methodological approach, accepted in the leading countries, which was adapted for the real mining and technical conditions of sites in the Republic of Bulgaria. (Project 2000-10, Fund "Labour conditions" - MLSP "Update of the regulatory framework for blast-seismic protection").

The open pit mines "Medet", "Assarel" and the quarry "Lyulyakovitsa" were used as a base for monitoring the research of the seismic impact of the blasting operations.

Detailed instrumental surveys have been performed for determination of the dependence, characterising the parameters of the blast-induced seismic impact at the following areas:
- in the generation zone - in the rock medium, next to the borders of the blast field - the working floor;
- in the area of distribution - in the rock massif between the blasting field and the registration point (the protected object).

Graphically, the dependence is expressed in a logarithmic scale on the axes "X" and "Y" "Registered vibration velocity - Adjusted distance" PPV = f (R*Q^2); PPV = f (R*R*Q^3);

The research includes the blasting of:
- charges of a full camouflet action;
- drill-holes with full technological mass of the charge.

The research also includes control measurements to examine the level of vibrations generated during test blasts and technological blasts.

The seismic impact generated by blasting in the different areas of blastability and in the area next to the protected sites has been studied (Mikov, 2010b, Shishkov, 2019). The seismic receivers were located in profiles, distributed from the place of generation to the protected object.

The adopted methodological approach was "reduction of the specific consumption (sc. charge concentration) of explosive per linear meter of blasted mine mass" by researching the dependence of the blasting effect on the geometric parameter "spacing between boreholes", as well as studying the relative consumption (sc. specific charge) of explosive for extraction and crushing of tons of mine mass. (q, kg/t). This consumption is subordinated to the geometrical parameters of blasting – maximal burden (sc. average) for the drill-holes of the first row, spacing between the boreholes in the row, burden between the drilling rows.

This was achieved by designing and performing a blasting test in a zone, determined by blastability, while maintaining consistency in:
- the acreage of the blasting field in accordance with the development of the mining works on the defined section;
- diameter of the boreholes;
- energetic parameters of the explosive charge in the drill hole - number of the charges, length of the main and upper charge; length of the intermediate stemming; length of the upper stemming; schedule of commutation of the charges in time and space.

The organisation of the preparation of the blasting field and the implementation of the test blasting was in accordance with the established practice of the copper mine, where the test took place.

The actual parameters of the blasting were determined when loading the boreholes.

After the blasting operations, an expert engineering assessment of the explosive effect was made by viewing the blasted pile. The grain size distribution of the crushed mine mass (percentage of oversized rock fragments and average piece size) were observed.

The excavation of the material was also carefully monitored. After the digging of the material, repulsion (ejection) of the rock massif was documented at the level of the floor and in the contour of the blasting field.

The quantitative indicators of the test blasting - extraction of mining mass per linear meter of drilling and relative consumption of explosive was determined.

Results of the performed research

To assess the blast-induced seismic impact on the structures of CPT-3, a series of blasting operations were performed and the parameters of the blast-seismic effect in a rock massif in the area of the foundation of the CPT-3 facility were registered (Fig. 1).

Fig. 1. Registered parameters of blast-induced seismic effect in a rock massif in the area of the foundation of CPT-3 facility

The dependence "reduced distance - registered velocity of blast-induced seismic vibrations" in the rock massif at the base of the foundation and in the reinforced concrete column foundation was derived from the software of the equipment (Fig. 2).

The analysis of the registered velocity of the blast-induced seismic vibrations in the rock medium and in the foundation (Fig. 3), confirms the expected logical dependence for the propagation of the impact on the rock massif in the base of the foundation to the structure.
Fig. 2. Registered parameters of blast-induced seismic effect, registered in the base of the foundation of facility CPT-3

The level of the blast-induced seismic impact is repeatedly lower than the calculated value of the guideline velocity of blast-induced seismic vibrations for the real acoustic and wave-conducting properties of the rock massif in the zone "Generation - Propagation from the explosive field to the protected facility" (Fig. 4).

Conclusions

The main conclusion is that the level of impact generated by the technological blasting on the reinforced concrete steps of the column foundation of CPT-3 is completely safe for the integrity of the structure of the facility. It is expedient, the monitoring of the blast-induced seismic impact in the area of the site to continue in order to collect sufficient data on the required reliability.

The results of the research are a base for recommendations for recalculation of the blast-induced seismic parameters of technological blasting for the protection of:
- rock massifs in the non-working and working benches and banks (bench faces);
- structures of built constructions near and inside pits of the open pit mine.

The studies were performed with consistency in the geometric and energetic parameters of the technological blasting in the different zones of blastability to achieve maximum explosive effect and length of the main charge (length limiting overcoming the technological burden and ejection of the deducted designed volume of mine mass) l = 8,0 m

For a certain blasting field, the main indicator characterising the rock massif in terms of blastability - relative consumption of explosive was determined.

In case of a change of the physical and-mechanical, acoustic and wave conducting properties and structure of the rock massif, it is necessary to update the D & B technology. The organisation, preparation and execution of technological blasting generate controllable parameters of the side impact of the explosion on the rock massif and the engineering facilities located in the area, to a safety level for the provoked plastic deformations and the human body.

References

Mitkov, V., Genchev, G., 2009. Determination of the safe distances for window glasses of buildings during detonation of makeshift explosive devices. – Annual of the University of Mining and Geology "St. Ivan Rilski", 52(2), 157–162. (in
EFFECTS OF THE IRON OXIDATION AND PRECIPITATION PROCESSES ON THE ARSENATE SORPTION AND COPRECIPITATION

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ABSTRACT. The main aim of this study was to assess the effects of ferrous iron oxidation, hydrolysis and precipitation of the ferric iron on the mechanisms of arsenate removal from acid mine drainage. The study was realized at the pH range 2.0 – 6.5. H2O2 was the oxidant used in the chemical test. A mixed culture of mesophilic iron-oxidizing chemolithotrophic bacteria (Acidithiobacillus ferrooxidans, Leptospirillum ferrooxidans) carried out the ferrous oxidation in the biological test. NaOH was used as an alkalinizing agent which triggered the ferric iron hydrolysis and precipitation. The results showed that the total content of retained arsenic by ferric iron hydrous oxides and its speciation as geochemical fractions depended on the iron and phosphate concentrations in acid solution. The results showed that phosphate concentration lower than 6 mg/L limited the ferrous iron oxidation rate. At the tested experimental conditions, arsenic sorption by formed ferric iron hydrous oxides was the main mechanism for its removal from acid mine drainage, as the ratio between iron and phosphate determined the proportions between the geochemical fractions of scavenged arsenic.

Keywords: arsenate, ferric iron, ferrous iron oxidation, sorption, fractions

Introduction

Arsenic is a metalloid and it ranks 20th position among the most abundant chemical elements in the earth crust. The toxic element is a part of about 200 minerals that occur naturally usually as sulfides, arsenides, and oxides, closely related to igneous and sedimentary rocks (Bowell et al., 2014). Apart from pyrite/ sulfide oxidation, processes of reductive dissolution of iron minerals, arsenic desorption at pH higher than 7.0, and geothermal process lead to the natural release of the element to water (Ali et al., 2018).

Arsenic occurs in natural waters both in organic and inorganic forms, as the arsenite, As(III), and arsenate, As(V). Arsenic is similar to its predecessor in group, phosphorous, but processes of oxidation, reduction, methylation play a significant role in its biogeochemical cycle. Based on close similarity between arsenate and phosphate, strong competitiveness exists between ions in the processes of adsorption-desorption processes, ion-exchange, solid-phase precipitation and biological uptake. However, the regular exposure to arsenic compounds causes adverse health effects like diabetes, neurological abnormalities, arteriosclerosis, renal effects, cardiovascular dysfunction, and carcinogenic risks in human beings (Abdul et al., 2015). For that reason, arsenic and arsenic compounds are included in group 1, carcinogens to humans, according to the International Agency for Research on Cancer (IARC). That was the reason the water standard of arsenic set by the Environmental Protection Agency (EPA) and recommended by the World Health Organization (WHO) to be reduced from 50 μg/L to 10 μg/L (WHO, 2001).

The previous studies have shown that goethite (α-FeOOH) possesses higher adsorption capacity and it removed arsenate more efficiently from spring waters both in batch and continuous way of operation in comparison to hematite (α-Fe2O3) (Zheleva et al., 2016; Zheleva and Georgiev, 2019). The leaching tests revealed that arsenate adsorbed mostly specifically with inner-sphere complexes formation between adsorbate and the mineral surface.

To study the role of processes of ferrous iron oxidation, hydrolysis and precipitation of generated ferric iron on the arsenic removal mechanisms at acidic pH was the main aim of this article.

Materials and methods

The effects of ferrous iron oxidation and ferric iron hydrolysis at acidic pH on the arsenic sorption/ precipitation were studied by batch tests. The study was carried out in polypropylene flasks with screw caps. A thermo-shaker provided a constant temperature (35°C for the bacterial oxidation, 55°C for the chemical oxidation) and agitation (200 rpm) during the tests. Hydrogen peroxide was used as a chemical oxidant in the abiotic test, while the process of the biological oxidation of ferrous iron was studied by a mixed culture of acidophilic iron-oxidizing chemolithotrophic bacteria consisted of Acidithiobacillus ferrooxidans and Leptospirillum ferrooxidans, (~6x107 cells/ mL). The mixed culture was isolated from a copper slag deposit. The nutrient solutions for their growth contained the following salts (in g/L): (NH4)2SO4 – 0.4; MgSO4·7H2O – 0.4; KH2PO4·3H2O – 0.056; and FeSO4·7H2O – 14.9 (Tuvinen and Kelly,1973). Sulfuric acid solution (30%) buffered pH in the range of 1.8-1.9. The prepared acidic solution was spiked with arsenate (as K2HAsO4), so the concentration of toxic element was 250 μg/L. The ferric iron hydrolysis was triggered by manual addition of sodium hydroxide (1.0 N solution) periodically. The rate of oxidation, ferric iron precipitation, and arsenic sorption/ coprecipitation was studied by in situ measurements of pH, Eh, and sampling.

The ferrous iron concentration was calculated from the difference between the total iron and ferric iron concentration during the tests. The ferrous iron oxidation rate, g Fe2+/(L.h) was calculated according to that equation:

\[ \text{Fe}^{2+}_{\text{oxidized}} = \frac{\text{Fe}^{2+}_{\text{in}} - \text{Fe}^{2+}_{\text{out}}}{(t+n - t)} \]

where Fe2+in and Fe2+out denote the ferrous concentration at the respective hour from the beginning of the test.

The samples were stored in a refrigerator at 8°C till analyses. The test duration was 75 hours. All experiments were performed in triplicate. The concentration of ferric iron and total iron in the samples was determined by a spectrophotometric method in the presence of sulfosalicyclic acid at acidic and
alkaline pH, respectively. The arsenic and phosphate concentrations were measured using a spectrophotometer MERCK SQ22 at 820 nm and a 20 mm cuvette (Johnson and Pilson, 1971).

Effect of the initial iron concentration on arsenate sorption/ co-precipitation at acidic pH

This effect was studied using a solution with content similar to that of the above-mentioned solution. The only difference between the variants was the initial iron concentration: 2.2, 1.7, 1.2, and 0.9 g/L, respectively.

Effect of the initial phosphate concentration on arsenate sorption/ co-precipitation at acidic pH

This effect was studied through tests with a solution similar to that of the above-mentioned solution. The only difference between the variants was the initial phosphate concentration: 18.3, 11.0, 6.6, and 3.3 mg/L, respectively.

A four-stage sequential extraction, based on that reported by Wenzel et al. (2001), was applied to the iron-contained residues deposited at the end of oxidation tests. The following arsenic factions were determined: 1) exchangeable (extracted with 0.05 M (NH₄)₂SO₄ for 4 h); 2) specifically surface-bound (extracted with 0.05 M NH₄H₂PO₄ for 16 h); 3) capsulated in amorphous iron hydrous oxides (leached with 0.2 M ammonium oxalate buffer (pH 3.0), in dark for 4 h), and 4) capsulated in crystalline iron hydrous oxides (extracted with 0.2 M ammonium oxalate buffer (pH 3.0) and 0.1 M ascorbic acid for 30 min at 90°C). The extracts from third and fourth fractions were treated before the arsenic analysis with UV light and H₂O₂ in a 70% UV Digester, Methrohm for organic degradation and iron hydrolysis. The dropwise addition of 4N HCl dissolved the iron precipitates that had deposited on the bottoms’ tubes. The total content of arsenic in the iron hydrous oxides residues was determined in the nitric acid’s extract.

Results and discussion

The main characteristics of acid mine drainage generated as a result of oxidation of sulfides, both biological and chemical, are acidic pH, higher concentrations of iron, aluminium, sulfates as well as substantial concentrations of non-ferrous metals (copper, zinc, nickel, etc.) and toxic elements (arsenic, uranium, etc.). Treatment of acid mine waters, both by active or passive methods, is based on the selective removal of each pollutant through a suitable alternation of oxidation, neutralization, precipitation processes in some cases, and precipitation. The process of oxidation plays a crucial role in iron removal because a higher portion of the chemical element in acid mine drainage is in a ferrous state. The bacterial oxidation of ferrous iron plays the main role at acidic pH because the chemical oxidation by dissolved oxygen carries out with negligible rate at pH lower than 3.5. That process was studied by a mixed mesophilic iron-oxidizing chemolithotrophic bacteria which use ferrous iron as a donor of electrons in their metabolism while the final acceptor of electrons is the molecular oxygen:

\[ \text{Fe}^{2+} + \frac{1}{2} \text{O}_2 + 2\text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O} \]

However, the iron-oxidizing bacteria yield a low amount of energy from that reaction which bacteria compensate by a higher rate of the substrate utilization (Silverman and Lundgren, 1959). For that reason, the rate of ferrous iron oxidation during the first 20 hours of the test was in the range of 0.03 – 0.04 g Fe²⁺/(L·h) despite the still low number of bacterial cells (Table 1). The ferrous iron oxidation is an acid-consuming process also and pH increased from 1.9 to above 2.15 during that period. Due to the gradual increase the bacterial cells, the rate of ferrous iron oxidation increased further up to 0.11 g Fe²⁺/(L·h) between 50 – 62 hours (Table 1). After that period of the test, ferrous iron concentration was too low which determined the sharp decrease in its rate of oxidation. Almost the same highest rate of bacterial ferrous iron oxidation was measured when the initial ferrous iron concentration varied in the range of 0.9 – 3.0 g/L (Table 2). The only difference was the total duration of the test needed to oxidize ferrous iron to the ferric state. In that case, the test’s duration decreased from 75 to 30 hours.

Abiotic ferrous iron oxidation was carried out in the presence of hydrogen peroxide as the needed amount was calculated according to this reaction:

\[ 2\text{Fe}^{2+} + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + 2\text{H}_2\text{O} \]

Trends in changes of pH, concentrations of ferric and total iron were similar to those already noticed in tests with the bacterial oxidation (Figure 1). However, chemical oxidation has an advantage because it could be realized with a rate significantly higher than the rate measured in the presence of bacterial cells. After all, the process could take place in a reactor at higher temperatures and the needed amount of oxidant could be added in a very short period.

The gradual addition of an alkalinizing agent (sodium hydroxide in that case) during the ferrous iron oxidation triggered the processes of ferric iron hydrolysis and precipitation. That was an acid-generating process that equilibrated with the acid-consuming character of the ferrous iron oxidation. That was the reason for buffering pH in the range of 2.2 – 2.4 between 22 and 58 hours of the test (Table 1).

Table 1. Bacterial oxidation of ferrous iron by acidophilic iron-oxidizing bacteria and the effect of sodium hydroxide addition on the ferric iron precipitation

<table>
<thead>
<tr>
<th>Time, h</th>
<th>pH</th>
<th>Fe³⁺, mg/L</th>
<th>FeAl₃, mg/L</th>
<th>Consumption of NaOH, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.92</td>
<td>18</td>
<td>3050</td>
<td>0</td>
</tr>
<tr>
<td>22</td>
<td>2.15</td>
<td>880</td>
<td>2955</td>
<td>0</td>
</tr>
<tr>
<td>26</td>
<td>2.27</td>
<td>920</td>
<td>2945</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>2.31</td>
<td>865</td>
<td>2760</td>
<td>0</td>
</tr>
<tr>
<td>34</td>
<td>2.30</td>
<td>825</td>
<td>2540</td>
<td>9.7</td>
</tr>
<tr>
<td>42</td>
<td>2.28</td>
<td>710</td>
<td>2200</td>
<td>53.2</td>
</tr>
<tr>
<td>50</td>
<td>2.23</td>
<td>615</td>
<td>1955</td>
<td>184.8</td>
</tr>
<tr>
<td>54</td>
<td>2.46</td>
<td>425</td>
<td>1320</td>
<td>763</td>
</tr>
<tr>
<td>58</td>
<td>1.55</td>
<td>220</td>
<td>656</td>
<td>774</td>
</tr>
<tr>
<td>62</td>
<td>3.33</td>
<td>16</td>
<td>20</td>
<td>786</td>
</tr>
<tr>
<td>64</td>
<td>3.95</td>
<td>5.5</td>
<td>11</td>
<td>79.2</td>
</tr>
<tr>
<td>70</td>
<td>6.14</td>
<td>0.0</td>
<td>4.2</td>
<td>109.6</td>
</tr>
<tr>
<td>75</td>
<td>6.52</td>
<td>0.0</td>
<td>1.5</td>
<td>28.2</td>
</tr>
</tbody>
</table>

It is well-known that ferric iron precipitate at acidic pH mainly as poorly crystalline hydrous ferric oxides minerals as sulfate-containing schwertmannite [FeₓO₄(OH)₆SO₄], jarosite [MFe₃(SO₄)₂(OH)₆, where M is usually H₂O⁺, K⁺, Na⁺ or NH₄⁺], as well as goethite (Wang et al., 2006). The key factors controlling the mechanism of iron precipitation are pH,
concentrations of ferric iron, sulfates, and monovalent cations (H⁺, K⁺, Na⁺):

\[
8\text{Fe}^{3+} + 14\text{H}_2\text{O} + \text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2\text{O}_3(\text{OH})_2\text{SO}_4 + 24\text{H}^+
\]

\[
\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{FeOOH} + 3\text{H}^+
\]

Fig. 1. Chemical oxidation of ferrous iron through multiple additions of hydrogen peroxide at 55°C

In the beginning, mostly in the case of bacterial oxidation, the colour of the solution turned into deep red which was an indication for the building up of ferric iron in the solution and its partial precipitation as jasperite mainly. However, the alkalizing agent was added at regular intervals during the test so that the ferric iron concentration never exceeded 1000 mg/L and redox potential (Eh) of the solution measured was always lower than + 600 mV. Those experimental conditions provoked goethite formation mainly as a result of ferric iron hydrolysis. For that reason, the ferric iron concentration decreased significantly between 26 and 62 hours and the colour of precipitate deposited at the flask bottom turned in yellow-orange. The main advantages of goethite in comparison to jasperite and schwertmannite are a lower value of sludge volume index and higher settling velocity (Georgiev et al., 2017), while the values of properties as surface area and sorption capacity are comparable (Cornell and Schwertmann, 2003). For that reason, goethite is still one of the final products preferred during the iron removal processes at an industrial scale.

Table 2. Effect of the chemical oxidation of ferrous iron and the ferric iron precipitation on the final arsenic concentration at the test’s end

<table>
<thead>
<tr>
<th>Initial content of ferrous iron, g/L</th>
<th>The maximum rate of bacterial oxidation of ferrous iron, g/L.h</th>
<th>Total consumption of NaOH, g/L</th>
<th>Final As concentration, μg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,0</td>
<td>0.15 – 0.16</td>
<td>2.78</td>
<td>4.7</td>
</tr>
<tr>
<td>2,2</td>
<td></td>
<td>2.06</td>
<td>4.8</td>
</tr>
<tr>
<td>1,7</td>
<td></td>
<td>1.65</td>
<td>5.6</td>
</tr>
<tr>
<td>1,2</td>
<td></td>
<td>1.24</td>
<td>8.2</td>
</tr>
<tr>
<td>0,9</td>
<td></td>
<td>0.91</td>
<td>9.6</td>
</tr>
</tbody>
</table>

The higher amount of sodium hydroxide was added between 40 to 60 hour since the test’s start when more than of 2.0 g/L ferric iron had precipitated and the average iron removal rate was in the range of 0.08 – 0.1 g Fe_{eq}/(L.h) (Table 1). The highest rate of bacterial ferrous iron oxidation was measured in the same stage of the test which revealed the positive effect of ferric removal (the end product of bacterial metabolism) on ferrous iron utilization.

The precipitation of ferric iron consumed 2.79 g/L sodium hydroxide totally which led to increasing pH almost to neutral point (Figure 2). Almost 90% of that amount has consumed for buffering pH in the range of 2.2-3.3. The same trend of an alkalizing consumption was noticed in the tests where the initial concentration of ferrous iron decreased gradually from 3.0 to 0.9 g/L. In those cases, the consumed amount gradually decreased to 0.91 g NaOH/L for the variant with the initial ferrous iron content of 0.9 g/L (Table 2). The amount of sodium hydroxide (2.62 g/L) consumed in the abiotic test was in the same range as the biotic test with an initial ferrous iron content of 3.0 g/L. The only difference was the rather shorter duration of the abiotic test (Figure 1).

The ferric iron precipitation was an efficient process for arsenic removal contained in the acidic solution. Two main processes have a role for arsenic removal at such conditions (acidity pH, a higher concentration of iron, ferric iron hydrolysis). Arsenic coprecipitation with ferric iron is one of the processes that could take place and it carried out in acidic effluents with higher arsenate concentration where the molar ratio between iron and arsenic is in the range lower than 10:1. The distinguishing feature of that process is linearity between iron and arsenic removal. Arsenate sorption on the surface of already precipitated poorly crystalline hydrous ferric oxide is the second process which is typical for acidic effluents with a substantial lower molar ratio of Fe/As. The distinguishing feature of that process is that arsenate removal carried out with a delay in comparison to iron removal. The results about arsenate removal showed that the process carried out at an almost constant rate and with some delay in comparison to the periods with the highest iron removal rate (Figure 3). For example, the rate of ferric iron precipitation during the first 15 hours of bacterial oxidation of ferrous iron was too low which determined the very low rate of arsenate removal too. The rate of arsenate removal increased significantly to 10 μg/L (L.h) at 30 hours when already approximately 8.5% of the initial iron content had precipitated. It is interesting to note that during the next 20 hours of the test, pH buffered in a very narrow range (2.23 - 2.31) with
an almost constant rate of iron precipitation. At such a condition, the rate of arsenate removal decreased twice despite the precipitation of another 25% of the iron in solution. The higher rate of arsenate removal (15.2 μg/(L-h)) was measured after 58 hours, when the rate of iron precipitation reached over 0.1 g/(L-h), despite the substantial acidification of the solution to 1.6 (Figure 3).

The observed trend of arsenate removal revealed that the sorption of the toxic element by poorly crystalline hydrous oxides was the main process carried out at those conditions. It is interesting to note, that adsorption of such lower concentration arsenic took place in an environment where sulfate concentration was more than 7 g/L, which revealed that arsenate competes with sulfate very effectively toward active sites of ferric iron hydrous oxides.

The higher rate of arsenate removal observed at lower pH (1.6, 58 hour, Figure 3) could be explained by the higher surface area, which the hydrous ferric oxides possess, and their significant sorption capacity to anions due to the presence of the pH-dependent surface. In highly acidic conditions, the pH-dependent surface charge of minerals is positive due to the protonation of surface situated hydroxyl groups. The existence of surface positive charge determines two different mechanisms of arsenate adsorption – non-specific (exchangeable) and specific. The non-specific adsorption relies on an electrostatic bond formation between the charged particles and there is no substantial reduction of their energy due to the outer-sphere complexes formation. For that reason, the process of desorption carried out at a higher rate in the presence of competitive ion. The specific adsorption relies on a chemical bond formation between the charged particles and with a substantial reduction of their energy due to the inner-sphere complex formation. This kind of adsorption is a result of ligand exchange mechanism toward a surface situated hydroxyl or sulfate group:

\[
\text{FeOOH} + x \text{H}^+ + n \text{H}_2\text{AsO}_4\rightarrow \text{FeOH} + n\text{AsO}_4^{2-} + x \text{H}_2\text{O}
\]

For that reason, the desorption process, in that case, carry out only after significant changes in environmental conditions (as pH, Eh, etc.) which enhances the bond’s breaking.

The tests with different initial ferrous iron content revealed that it hadn’t an effect on the final arsenate concentration (Table 2). In all tested variants, where the molar ratio Fe/As ranged from 18000:1 (with 3.0 g/L initial Fe content) to 5333:1, the final arsenate concentration was lower than 5 μg/L. This revealed that the poorly crystalline hydrous ferric oxides possessed surface area and sorption capacity sufficient to adsorb arsenic at acidic pH.

**Table 4. Arsenic fractions in iron oxyhydroxides precipitated due to the bacterial oxidation of ferrous iron and hydrolysis**

<table>
<thead>
<tr>
<th>Index</th>
<th>Bacterial oxidation of ferrous iron at:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe(II)</td>
</tr>
<tr>
<td></td>
<td>3.0 g/L and PO₄³⁻</td>
</tr>
<tr>
<td></td>
<td>PO₄³⁻</td>
</tr>
<tr>
<td>mg/L</td>
<td>30.5</td>
</tr>
<tr>
<td></td>
<td>mg/L</td>
</tr>
<tr>
<td></td>
<td>0.082</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Arsenic fractions, %</td>
<td>Exchangeable, %</td>
</tr>
<tr>
<td></td>
<td>Specifically adsorbed, %</td>
</tr>
<tr>
<td></td>
<td>Co-precipitated by amorphous iron oxides, %</td>
</tr>
<tr>
<td></td>
<td>Co-precipitated by crystalline iron oxides, %</td>
</tr>
<tr>
<td></td>
<td>Residual, %</td>
</tr>
<tr>
<td></td>
<td>Total content, μg/g (%)</td>
</tr>
</tbody>
</table>

Scorodite formation (FeAsO₄·2H₂O) is an example of arsenate coprecipitation with iron as the final concentration of toxic element is lower than 10 μg/L (Singhania et al., 2005). That process is used in the treatment of industrial effluents with very high arsenic concentration and the maintenance of appropriate conditions (a higher temperature and seeding rate) provokes the scorodite formation. At lower temperatures, for example in the weathering zone of mineral deposits, arsenic precipitate as its amorphous counter-parts (FeAsO₄·xH₂O). Scorodite is stable at acidic pH while at higher values it transforms to goethite with concomitant release of arsenate (Dove and Rimstidt, 1985). Such evidence of the redissolution of arsenate wasn’t observed in the study even though the process of neutralization was carried out almost to neutral point (Figure 3).

Besides the arsenate adsorption, the ferric iron oxyhydroxides removed very efficiently phosphates also (Figure 3). It is well-known that arsenic and phosphorus belong to the same group which determined their chemical similarities as well
as strengthens competitiveness between both elements for the adsorption positions, especially at neutral and slightly alkaline pH (Frau et al., 2008). However, the curves of arsenate and phosphate removal didn’t reveal an effect of competition between both anions. It could be explained with the different processes which took place for their removal - arsenate adsorption on the surface of poorly crystalline hydrous ferric oxides and phosphorus coprecipitation with iron (probably as FePO₄·2H₂O), respectively. Regarding the phosphorus removal, the molar ratio of Fe:PO₄ during the tests ranged from 16 (at 30.5 mg/L initial phosphate content) to 1600 (at 3.0 mg/L initial phosphate content) as the phosphate coprecipitation with iron was quite possible at higher initial phosphate concentration. It is well-known that ferric phosphate is virtually insoluble and at strongly alkaline pH converses to ferric hydroxide (Robins et al., 1991).

The bacterial activity at mine deposits depends on several important environmental factors as the concentrations of available forms of phosphorus and nitrogen are among the most frequently limiting (Tuovinen et al., 1971). Phosphorus is an element, essential for life which plays a crucial role in the storage of energy, the structure of cell membranes, and the encoding of genetic information. For that reason, the effect of phosphate concentration on the rates of ferrous iron oxidation and arsenate removal was studied by a set of tests. The results showed that a phosphate concentration higher than 11.0 mg/L, the rate of bacterial ferrous iron oxidation was almost the same as that measured when phosphate concentration was 30.5 mg/L (Table 3). When the initial phosphate concentration dropped further to 3.0 mg/L, the ferrous iron oxidation rate decreased almost twice. It revealed the strong limiting effect on the bacteria which phosphate had when the environment was deficit toward that nutrient. Regardless of the lower rate of bacterial ferrous iron oxidation, the total consumption of sodium hydroxide for ferric iron precipitation was in a narrow range. Most likely in the tests where the phosphate was in deficit, some part of the ferrous iron was oxidized chemically with molecular oxygen due to the regular addition of the alkalinizing agent and the existence of microzones with alkaline pH for a very short period. However, the arsenate removal at all tested phosphate concentration was a very efficient process as about 98.2% of the initial amount was sorbed by the ferric iron oxyhydroxides and the residual arsenate concentration was always lower than permissible concentration.

The applied arsenic fractionation by sequential leaching revealed the strong effect of studied factors on the toxic element speciation. First of all, the arsenic’s total content retained by the ferric iron hydroxide oxides varied in a narrow range in all variants where the initial ferrous iron content was the same (Table 4). When the initial ferrous iron concentration decreased from 3.0 to 0.9 g/L, the retained arsenic’s total content increased considerably and reached 126.5 μg/g. At such conditions, more than 50% of that amount was an exchangeable fraction, i.e. a fraction formed due to non-specific adsorption of hydrous ferric oxides and mobilizing easily in an environment with a higher concentration of competitive anions, such as sulfate. The insignificant content of specifically adsorbed arsenic (6.5 %) revealed that its retention during ferric iron precipitation had carried with intense competition with available phosphate. When the arsenic retention was carried out in an environment with a lower concentration of phosphate (which is a case type for the mine sites), the content of specifically adsorbed arsenic increased on account of the lower content of arsenic presented as an exchangeable fraction. The arsenate encapsulation in the hydrous iron oxides lattice was the next step in the toxic element removal at acidic pH. The poorly crystalline hydrous ferric oxides, which had precipitated at the very beginning of the process, acted as seeds during the ferric iron hydrolysis and following crystal’s growth. In this way, the initially adsorbed arsenate on the surface of hydrous ferric oxides had covered by the new layers of precipitates, and the process ended with encapsulation of the toxic element within the crystal lattice of deposited iron oxide. In that way, the reducible fraction of heavy metals and toxic elements in the solid samples formed (Tessier et al., 1979). In that case, the reducible fraction of arsenic in freshly deposited ferric iron oxides was specified in two subfractions - arsenic capsulated in amorphous and arsenic capsulated in crystalline iron oxides, respectively (Table 4). The distinction between those subfractions was determined by the redox conditions at which redoxylation of the toxic element contained minerals took place. Both processes lead to arsenic release and re-dissolution. The arsenic capsulated in the amorphous iron oxides were significantly higher than the arsenic capsulated in the crystalline counterpart. The reason was the lower temperature and atmospheric pressure at which ferric iron precipitation took place. The concentration of iron and phosphate in mine waters had a strong effect on arsenic encapsulation in the deposited hydrous iron oxides as the lower iron content (0.9 g/L) and higher phosphate content (30 mg/L) determined the lowest percent of that fraction (20%, Table 4).

Conclusions

1. The results showed that the rate of bacterial ferrous iron oxidation was constant for the tested ferrous iron concentration range, while the rate decreased significantly when the phosphate concentration was lower than 6 mg/L.

2. Arsenate adsorption processes on the surface of poorly crystalline hydrous ferric oxides and their further growth due to ferric iron precipitation were the primary mechanism for arsenic removal from acid mine waters. As a result of that process, the residual arsenic concentration was lower than maximum permissible water levels (10 μg/L), regardless of the ratio between iron to arsenic.

3. The iron content, phosphate content, and iron to phosphate ratio in acid mine drainage substantially affected the total amount of arsenic retained by ferric iron hydrous oxides and the proportions between the geochemical fractions of the toxic element.

Acknowledgements. The authors would like to express their gratitude to the Scientific Research & International Partnership Unit of the University of Mining and Geology “St. Ivan Rilski”, Sofia (under the frame of the GPF-229/2020 project) for the financial support for publishing of this article.

References


TREATMENT OF SULPHATES-RICH SOLUTIONS THROUGH ETTRINGITE PRECIPITATION WITH INDUSTRIAL REAGENTS

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ABSTRACT. Mine wastewaters are often characterised with high concentrations of sulphates, heavy metals and increased electrical conductivity. It is mandatory for the industry to implement convenient treatment methods in order to reduce these parameters. The aluminium precipitation with the simultaneous formation of ettringite was chosen for laboratory testing as it is appropriate when the concentrations of sulphates have to be reduced up to 300 mg/l according to the Bulgarian regulatory framework. In the present study synthetic waters were treated, as their composition was similar to that of typical mining effluents. Initially, the pH of the solutions was adjusted to 9.0 with Ca(OH)₂ and thus the heavy metals precipitated in the form of hydroxides. Then, an aluminium source was added as Al-cement, industrial Na-aluminate or aluminium oxychloride. The best results in terms of sulphates and electrical conductivity decrease were obtained with Al-cement (99 – 100 % sulphates removal rate), but the quantities of the generated sludges were large, which raises the question of their proper disposal. With the industrial Na-aluminate the rate of removal of sulphates was very low and with AlOCl it was 96%. However, the use of both reagents showed an increase in the electrical conductivity of the treated solutions.

Keywords: ettringite, sulphates, removal

Introduction

At the mined sites with sulphide ores and during the processing of mining waste sulphide oxidation often occurs with the relevant negative impacts on water bodies - reduction in water quality (Bowell, 2004). Sulphates are produced from the exposition of pyritic rocks to air during mining activities (Liang et al., 2015). Thus, sulphate and acidity are formed (Equation 1).

\[2\text{FeS}_2(s) + 7\text{O}_2(g) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{Fe}^{3+}(aq) + 4\text{SO}_4^{2-}(aq) + 4\text{H}^+(aq)\] (1)

Effluents from mining industry are often characterised by sulphates, heavy metals and electrical conductivity above the permissible levels. It is mandatory for the industry to implement convenient treatment methods for the decrease of these parameters.

The damage caused by sulphite emissions is not direct, since sulphites are a chemically inert, non-volatile, and non-toxic compound. However, high sulphate concentrations can unbalance the natural sulphur cycle. Sulphite is often the dominant contaminant of mine water and can form a wide range of salts and provoke salinity (Bowell, 2000). The accumulation of sulphate-rich sediments in lakes, rivers and sea may cause the release of toxic sulphides that can provoke damages to the environment. Together with bicarbonates and chlorides they form a major part of anions in natural waters (Benatti et al., 2009).

The existing mining water treatment technologies are generally poorly documented and not easily applicable. The processes of chemical treatment with mineral precipitation are usually the cheapest, but they produce the largest amount of sludge. Subsequent sludge reduction or recycling technologies have to be applied.

Chemical precipitation, combines different methods, as the classical approach is based on formation of precipitates using chemical reagents. A widely used method for sulphates removal from water is their precipitation as insoluble sulphate salts. The minimum achievable concentration of sulphates depends on the specific salt formed. Suitable compounds for removal of sulphates from water and sludge formation are Ca, Ba and Al.

The addition of calcium hydroxide or calcium carbonate to water for sulphate removal in the form of gypsum (Equations 2 and 3) is an attractive method in many aspects - low cost, easily operable, sludge removal.

\[\text{Ca(OH)}_2(s) + \text{SO}_4^{2-} + 2\text{H}_2\text{O} (l) \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O}\] (2)

\[\text{CaCO}_3(s) + \text{SO}_4^{2-} + 2\text{H}_2\text{O} (l) \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O} + \text{CO}_2 + \text{H}_2\text{O}\] (3)

The main process deficiencies are the high solubility of calcium sulphate and existence of interfering ions in the wastewaters. Gypsum is slightly soluble in water \((K_{sp} = 3.14 \times 10^{-6})\) and the sulphate concentration can be reduced only to about 1500 mg/l. This is a significantly higher concentration than the permissible values for surface waters. Considering the relatively high sulphate levels remaining in the treated water even after reaction with lime or limestone, the process may be better suited as a pre-treatment step for acid mine waters.

Chemical treatment of mine waters using Ba salts has proved to be capable of removing sulphates to less than 250 mg/L (Śpaldon et al., 2017) A separation can take place by a precipitation with barium (Ba) added as BaCl₂, Ba(OH)₂, BaCO₃ or BaS (Bosman et al., 1990).

Bartle (BaSO₄) is highly insoluble making it an excellent candidate as a sulphate removal phase for sulphate treatment.

However, the Ba application is rather rare due to its limitations such as the high cost of the reagents, toxicity of barium salts and, in case of BaCl₂, the free Cl⁻ ion concentration after the formation of BaSO₄. If the concentration of sulphates has to be brought to lower level, aluminium precipitation with the simultaneous formation of ettringite is recommended. This results in low concentration of 50-100 mg/l sulphate as the ettringite is less soluble in water and can be used for removal (Pehlivanguoglu et al., 1998). Ettringite is much more insoluble in water \((K_{sp} = 2.8 \times 10^{-45})\) compared to gypsum and removal of sulphate by precipitating ettringite could consistently reduce the sulphate concentration (Liang et al., 2015; Bowell, 2004).

Kiessig and Kunze (1986) proposed simplified chemical equations of the formation of ettringite during the sulphate removal. The overall process is presented in Equations 4 – 6.

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74
Ca₃[(Al(OH)₆)₂·6H₂O]+6H₂O + Ca²⁺ + SO₄²⁻ →
Ca₃[(Al(OH)₆)]·6H₂O

pH 11.5 – 12.0: Ca₃[(Al(OH)₆)]·6H₂O + CaSO₄ →
Ca₃[(OH)₂(SO₄)₂]·26H₂O (5)

Ca₃[(Al(OH)₆)]·6H₂O + 3Ca²⁺ + 3SO₄²⁻ + 20H₂O →
Ca₃[(OH)₂(SO₄)₂]·26H₂O (6)

The ettringite precipitation requires more complex chemical conditions to form sludges. Thus, this technology is more complex to operate. The operating parameters such as molar rates of calcium to sulphate and aluminium to sulphate along with pH have a crucial effect on the sulphate removal efficiency (Aygun et al., 2018).

The ettringite formation and precipitation requires blending of the aluminium source and the pre-treated mine water at an appropriate mass ratio of Ca:Al:SO₄ for 30 to 300 minutes as a reaction time. In practice, an excess (20%) of aluminium in terms of the stoichiometric requirements is dosed to enhance kinetics to achieve low residual sulphate concentration. Lime addition is also required to maintain the process at the optimum pH. A saturated limewater is fed at a controlled rate to maintain a reactor target pH above 11.5. The optimum pH for ettringite precipitation has been found to be around 12.0 (Kabdagi et al., 2015). After the precipitation reaction is complete, the ettringite solids are separated from the feed water, filtered and thickened.

Due to the high sulphate removal efficiencies of 85-90% (Tolonen et al., 2016) and of over 95-98% (Fang et al., 2018) the ettringite precipitation is a recognised method, appropriate to be implemented in industrial water treatment facilities. Worldwide, two commercial processes with ettringite precipitation for mine waters with sulphate concentrations over 2000 mg/l are often used - the SAVMIN Process and the CESR Process - Cost Effective Sulphur Removal Process (Walhalla Process). They both include heavy metals precipitation and gypsum formation as preliminary treatment step.

In the present study three different industrial sources of aluminium were tested, added to artificial waters with composition similar to typical mining effluents in order to reduce sulphate concentration, electrical conductivity and heavy metals contents in the treated waters.

**Materials and methods**

For the present investigation laboratory tests were carried out in a periodic regime by lime (as a preliminary step) and ettringite precipitation in order to optimise the chemical processes.

In previous analyses of real waters from a copper mining site in the Srednogorie region, low pH values were detected (in the range of 3.5 - 5.0), which is a deviation from the regulatory requirements according to Ordinance H-4/2012. Increased values of other indicators - electrical conductivity, sulphates, iron, copper, arsenic and zinc were also found. It was decided for the synthetic solution used in this experiment to have a similar composition - Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.80</td>
</tr>
<tr>
<td>EC, mg/l</td>
<td>1780</td>
</tr>
<tr>
<td>Eh, mV</td>
<td>315</td>
</tr>
<tr>
<td>SO₄²⁻, mg/l</td>
<td>2000,00</td>
</tr>
<tr>
<td>Water hardness, meq/l</td>
<td>785,00</td>
</tr>
<tr>
<td>Fe total, mg/l</td>
<td>5,50</td>
</tr>
<tr>
<td>As, mg/l</td>
<td>0.02</td>
</tr>
<tr>
<td>Cu, mg/l</td>
<td>2.75</td>
</tr>
<tr>
<td>Mn, mg/l</td>
<td>1.75</td>
</tr>
<tr>
<td>Zn, mg/l</td>
<td>4.00</td>
</tr>
</tbody>
</table>

Table 1. Basic physical-chemical and chemical parameters of the synthetic solution

A different source of aluminium is added to the separate variants. Ettringite precipitation was achieved at molar ratios of Ca/S = 3.20 and Al/S = 1.25 stated for being optimal in the literature (Dou et al., 2017; Tian et al., 2019), as the final pH was adjusted to 11.6 ± 0.1 using Ca(OH)₂ solution (2%). Three different sources of Al – aluminium cement, industrial Na-aluminate and AlOCl were used. The treatment with industrial reagents involved stirring for 30 min and 30 min of precipitation. The mixing of samples was performed by magnetic stirrers at 700 rpm.

After each phase pH, EC and sulphate concentrations were measured.

The additional study was performed with use of different concentrations of aluminium cement (5, 10 and 15 g/l). The time for reaction was divided by two, as the first phase includes stirring for 30 min and 30 min of precipitation, and the second one - additional 30 min of stirring and 30 min of precipitation.

In this experiment, a third phase was included - recarbonisation using carbon dioxide and adjusting the pH to 6.5.

The concentration of sulphate in waters was determined using a spectrophotometric approach (with BaCl₂ as a reagent) at a 420 nm wavelength. Samples of effluents were measured for pH, electrical conductivity (EC) and redox potential. The concentrations of Fe, As, Cu Mn, Zn, Al and Ca in liquid samples were determined through ICP-spectroscopy.

Scanning electron microscopy (SEM-EDS) was performed in order to study the chemical composition of the sludges.

The volume of the precipitates was measured with conical flasks.

**Results and discussions**

**Preliminary treatment**

The treatment of water with lime is mainly aimed at the precipitation of heavy metals as hydroxides and part of the sulphate as gypsum. Due to the high solubility of gypsum, a reduction of EC to the necessary extent and sulphates could not be achieved (Table 2).

Data for the volume and weight of the formed sludge is presented in Table 3. The consumption of Ca(OH)₂ for neutralisation of the tested waters is estimated at 0.033 kg/m³ up to pH 9. The weight of the dewatered sludge is 0.13 kg at the lime treatment of 1 m³ of solution.
The chemical composition of the precipitates was obtained after they were examined with a scanning electron microscope equipped with a probe. The results are presented in Figure 1, as the elemental composition is presented in %. The sludge contains the heavy metals iron, copper, zinc, aluminium and manganese. From the data it can be concluded that the sludge is a mixture of different minerals, and iron is in the highest concentration among the heavy metals – 39.31%. Much of the sulphur is precipitated in the form of gypsum.

**Ettringite precipitation**

Ettringite precipitation was performed after removal of the sludge, produced from lime treatment. Additionally the pH was adjusted to 11.6 ± 0.1 using Ca(OH)$_2$ solution (2%). The quantity added from each of the Al-sources provides the optimal ratios Ca/S of 3.20 and Al/S of 1.25. The results obtained from the performed laboratory experiments with industrial reagents are presented in Table 4 and in Figure 2.

### Table 2. Chemical preliminary treatment for heavy metals precipitation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Initial value</th>
<th>Addition of 2% Ca(OH)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.80</td>
<td>9.00</td>
</tr>
<tr>
<td>EC, mg/l</td>
<td>1780</td>
<td>1717</td>
</tr>
<tr>
<td>SO$_4^{2-}$, g/l</td>
<td>2.00</td>
<td>1.997</td>
</tr>
<tr>
<td>Ca, mg/l</td>
<td>187.9</td>
<td>797.9±1.0</td>
</tr>
<tr>
<td>Fe total, mg/l</td>
<td>5.50</td>
<td>0.104±0.001</td>
</tr>
<tr>
<td>As</td>
<td>0.02</td>
<td>&lt;0.010</td>
</tr>
<tr>
<td>Cu</td>
<td>2.75</td>
<td>&lt;0.010</td>
</tr>
<tr>
<td>Mn</td>
<td>1.75</td>
<td>&lt;0.010</td>
</tr>
<tr>
<td>Zn</td>
<td>4.00</td>
<td>&lt;0.010</td>
</tr>
</tbody>
</table>

### Table 3. Parameters of the precipitates from 1l of treated solution with 2 % Ca(OH)$_2$ up to pH 9

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sludge volume, 30 min, cm$^3$</td>
<td>3.5 – 4.0</td>
</tr>
<tr>
<td>Sludge volume, 60 min, cm$^3$</td>
<td>5.5 – 6.0</td>
</tr>
<tr>
<td>Weight of the dried sludge, g/l</td>
<td>0.13±0.05</td>
</tr>
<tr>
<td>Consumption of 2% Ca(OH)$_2$, ml/l</td>
<td>1.65±0.02</td>
</tr>
</tbody>
</table>

Fig 1. Chemical composition in % of the precipitates after the preliminary treatment.
Table 4 shows that when using Al-cement 64% for sulphate removal was achieved, as the concentration of sulphate ions remained still slightly high. A decrease in the electrical conductivity of the solution was also observed.

Table 4. Sulphate removal with industrial reagents through ettringite precipitation (30 min stirring/30 min settling)

<table>
<thead>
<tr>
<th>Reagent per 1 l of treated solution</th>
<th>SO₄²⁻, g/l</th>
<th>Sulphate removal, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al–cement, 4 g/l</td>
<td>0.72</td>
<td>64</td>
</tr>
<tr>
<td>Na–aluminate, 2 ml/l</td>
<td>1.34</td>
<td>33</td>
</tr>
<tr>
<td>AlOCl, 3.4 ml/l</td>
<td>0.087</td>
<td>95.65</td>
</tr>
</tbody>
</table>

Industrial Na–aluminate (liquid product) is also strongly alkaline and raised the pH to 12.6, which leads to the need for pH adjustment. The sulphate removal was very low - only 33%.

When using AlOCl (aluminium oxychloride) a high rate of removal of sulphates was achieved - 95.65%, but the reagent use resulted in a decrease of pH values to 3.9. The correction of the pH to the optimal values of over 11.5 for ettringite precipitation requires significant amounts of lime solution. It was found that industrial sodium aluminate and AlOCl, due to the characteristics of the reagents, lead to a significant increase in EC of the treated solutions (Figure 2).

Table 5. Sulphate removal with industrial reagent Al-cement through ettringite precipitation

<table>
<thead>
<tr>
<th>Al-cement, g/l</th>
<th>Initial EC, mg/l</th>
<th>First cycle (60 min)</th>
<th>Second cycle (90 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>pH</td>
<td>EC, mg/l</td>
</tr>
<tr>
<td>5</td>
<td>1706</td>
<td>11.55</td>
<td>1378</td>
</tr>
<tr>
<td>10</td>
<td>1712</td>
<td>11.12</td>
<td>1349</td>
</tr>
<tr>
<td>15</td>
<td>1695</td>
<td>10.90</td>
<td>1389</td>
</tr>
</tbody>
</table>

Table 6. Parameters of the precipitates from 1 l of the treated solution at ettringite precipitation with Al-cement

<table>
<thead>
<tr>
<th>5 g/l Al-cement</th>
<th>Sludge volume, 30 min, cm³</th>
<th>100-110</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sludge volume, 60 min, cm³</td>
<td>250-260</td>
</tr>
<tr>
<td></td>
<td>Weight of the dried sludge, g/l</td>
<td>10,385</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>10 g/l Al-cement</th>
<th>Sludge volume, 30 min, cm³</th>
<th>220-230</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sludge volume, 60 min, cm³</td>
<td>300-310</td>
</tr>
<tr>
<td></td>
<td>Weight of the dried sludge, g/l</td>
<td>16,435</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>15 g/l Al-cement</th>
<th>Sludge volume, 30 min, cm³</th>
<th>440-450</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sludge volume, 60 min, cm³</td>
<td>340-350</td>
</tr>
<tr>
<td></td>
<td>Weight of the dried sludge, g/l</td>
<td>21,52</td>
</tr>
</tbody>
</table>

Table 7 shows that for copper, iron, zinc and arsenic completely satisfactory levels were achieved, but the waters were still characterised by high concentrations of aluminium. It should be borne in mind that the solubility of aluminium hydroxide is strongly dependent on pH and when the pH dropped to 6.5, the concentration of aluminium in the treated water decreases significantly.

Table 7. Parameters of water after ettringite precipitation (second cycle) and recarbonisation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>After ettringite precipitation with 5 g/l Al-cement</th>
<th>After recarbonisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>11,5±0,05</td>
<td>6,5±0,1</td>
</tr>
<tr>
<td>EC, mg/l</td>
<td>136±5</td>
<td>130±17</td>
</tr>
<tr>
<td>SO₄²⁻, g/l</td>
<td>0,03±0,008</td>
<td>0,046±0,010</td>
</tr>
<tr>
<td>Ca, mg/l</td>
<td>316±1,0</td>
<td>62,9±1,0</td>
</tr>
<tr>
<td>Fe total, mg/l</td>
<td>0,063 ±0,006</td>
<td>0,104±0,001</td>
</tr>
<tr>
<td>As</td>
<td>&lt;0,010</td>
<td>&lt;0,010</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;0,010</td>
<td>&lt;0,010</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;0,010</td>
<td>&lt;0,010</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt;0,010</td>
<td>&lt;0,010</td>
</tr>
<tr>
<td>Al</td>
<td>6,6±1,2</td>
<td>0,012±0,007</td>
</tr>
</tbody>
</table>

The composition of the precipitates includes Ca (35.99%), S (8.65%), Al (8.45%) and heavy metals – Fe (4.92%) and Cu (4.91%) (Figure 3).
Conclusions

The first step in the treatment of mining effluents rich in sulphate and heavy metals is liming. Thus, heavy metals and arsenic are effectively removed. The sludge formed contains gypsum and hydroxides of heavy metals. Due to the high solubility of gypsum, however, electrical conductivity and sulphates cannot be sufficiently reduced.

During the tested method of ettringite precipitation with industrial reagents, sodium aluminate and aluminium oxychloride cannot be used as the aluminium source. The best industrial reagents containing product derived from cement production is used. This results in terms of soluble of gypsum, however electrical conductivity and sulphates were measured. Due to the high solubility of heavy metals and arsenic are effectively removed. The sludge containing product derived from cement production is used. However, the quantities of sludge generated are larger, which raises the question of their proper disposal.

References


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CIRCULAR ECONOMY PRACTICES IN THE BULGARIAN RAW MATERIAL INDUSTRY

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ABSTRACT. The circular economy, which promotes the responsible and cyclical use of resources, contributing to sustainable development is becoming more and more popular, especially in the European Union. The concept of switching from the traditional linear to cyclical consumption model leads to minimisation of waste and environmental pollution, and in this regard the New Circular Economy Plan is already in place. The great ambitions for changes in the industry are strengthened by the Green Pact (Green Deal). The publication presents an in-depth study of the literature on the subject, as well as the five business models through which, in practice, a circle is realised. It has been established that the literature in the context of the mining industry is extremely scarce, and the business models through which the processes in the industry are carried out are poorly studied. An up-to-date survey of 13 companies in the raw-material sector in Bulgaria is also presented, aimed at showing the extent to which they understand and apply the circular economy in their work. The results unequivocally prove that the concept is not new for the business.

Keywords: circular economy, business models, raw material industry

Historical view of the term “Circular economy”

Today, the Circular Economy provides basic guidelines about what needs to be done to significantly and permanently reduce the resource dependence of the economy and to move towards overcoming the scarcity of non-renewable natural resources. It offers important solutions, especially related to production and design skills, new business models, cycle building skills, and cross-industry collaboration. The circular economy is a closed cycle covering each of the three areas: supply and responsible choice of producers, consumer demand and behaviour, and waste management (Europesworld, 2014).

The circular economy has different meanings for the different participants in various areas. Common denominators are waste design and pollution (waste reduction), maintenance of products and materials in use (increase in scale and keeping the value), regenerate natural systems, (loops, transition) and social aspect such as well-being (Ellen MacArthur Foundation, 2017).

Retrospectively, the term "circular economy" has a rich historical past on the basis of various schools of thought, such as "industrial ecology", "cradle to cradle", "efficient economy", "blue economy" and "bionimicry". The current meaning of the term is built on all of these concepts, each of which has contributed to its further improvement and development, such as "cradle to cradle", implies an endless cycle of the resource use, biomimetics or adaptation of naturally occurring forms in technology, natural capital - approach to environmental assessment, etc. All these concepts reinforce the idea of the circular economy, namely its goal - to extend the life cycle of resources by minimising the use of goods resulting in non-recyclable waste.

One of the founders of the idea is Alfred Marshall, who in 1890 introduced the concept of "Industrial Areas" - areas with high concentration of workers and companies specialising in the basic industry and auxiliary industries. Later, George Renner (1947) put in the term "industrial symbiosis," describing the exchange of residual materials as water and energy, and mentioning the possibility of companies exchanging waste as raw materials, describing the interrelationships that occur in nature as symbioses.

The first studies of the impact of consumer products on the environment appeared in the 1960s, mainly in a comparative context.

In 1966, Kenneth Boulding first introduced the concept of closed systems, envisaging a future economy that would function by reproducing the limited supply of waste and recycling waste.

The published Meadows's report (1972) "The Limits of Growth", underlines the limit of resources of the planet Earth. For the first time, a research team presented in this study scenarios based on computer modelling to stimulate interactions between populations, food production, industrial production, pollution and the consumption of non-renewable energy sources.

Despite its historical past, many scientists suppose that the term "circular system" was officially introduced into the economic model of Pearce and Turner (1990), who built their theoretical framework on the research of environmental economist Kenneth Boulding. In their study, Pearce and Turner offer a critical look at the traditional linear economic system and develop a new economic model that applies the principles of thermodynamics. In their paper "Economics of Natural Resources and the Environment" they outline the theories in and between the economics of natural resources and the implications for the concept of how the economy works. The authors consider the environment both as an entrance and as a receiver of waste. They indicate that neglecting the environment means ignoring the economy, as it is a linear or open system without a built-in recycling system. However, an extensive review of the literature over the last two decades has shown that the origins of the circular economy are rooted mainly in the environmental economy or in industrial ecology (Rizos et al., 2017).

Following Pearce and Turner, many authors have attempted to define the circular economy by providing resource-oriented definitions and / or interpretations, emphasizing the need to create closed circuits of material flows and reduce environmental impacts.

Thus, according to Preston (2012), "the circular economy is an approach that would transform the function of resources into the economy. Factory waste will be a valuable contribution to another process - and products can be repaired, reused or upgraded instead of disposed of".
Mitchell (2015) goes further and emphasizes the importance in the circular economy of conserving resources for as long as possible, as well as extracting maximum value from products and materials by using them for as long as possible and then recovering and using them again.

Sauvé et al. (2016) suggest that the circular economy refers to “the production and consumption of goods through a closed loop of material flows that internalise the external environmental impacts associated with the extraction of clean resources and the generation of waste (including pollution)”. According to them, the main focus of the circular economy is to reduce resource consumption, pollution and waste at every step of the product life cycle.

There are also several interpretations of the concept in the available literature that try to go beyond the concept of material resource management and include additional dimensions. For example, Heck (2006) argues that in the debate on the circular economy, the use of sustainable energy has not yet succeeded in gaining equal status compared to recycling and waste management. For this goal, he suggests that the transition to a circular economy will require tackling the challenge of establishing a sustainable energy supply, as well as taking decisive action in several other areas such as agriculture, water, soil and biodiversity (Rizos et al., 2017).

According to the Ellen MacArthur Foundation, the circular economy aims to redefine growth by looking beyond the current industrial waste model. The focus is on the benefits to society and on the gradual separation of economic activity from the consumption of limited resources, while reducing waste and ultimately projecting it outside the system. The circular model builds economic, natural and social capital, supported by the transition to renewable energy sources (Ellen MacArthur Foundation, 2017).

To facilitate the transition to an efficient circular economy, at the end of 2015 the European Commission adopted a package of measures to increase the global competitiveness of the European economy and protect limited resources, creating a level playing field for all actors. The package includes an action plan in the areas of product design, production processes, consumption, waste management, innovation and investment in plastics, food waste, raw materials, construction waste, biomass and legislative proposals on waste to reduce landfill, increase reuse and recycling.

The transition to a circular economy is a huge opportunity to transform our economy so that it is more sustainable and thus contribute to climate goals and the conservation of global resources, job creation and competitive development advantages for Europe. The transition to a circular economy will also help meet the goals set in the 2030 Agenda for Sustainable Development.

The new plan for a circular economy, which builds on what was achieved in 2015 - the European Green Pact, follows this trend. The green deal that gives a clear direction - a carbon-neutral and circular economy by 2050, and for this purpose it is expected to be adopted in the so-called Climate law. The focus on the circular economy is not accidental - 45% of the global greenhouse gas emissions are "invested" in products. These are the emissions during their production, as well as during the extraction and transport of the materials from which they are made (Paspaldzhiev, 2020).

Business models in the circular economy

The rapid deterioration of the world’s environment has led to the development of policies to reduce the negative impact of production and consumption. A number of countries have introduced acts and laws establishing the principle of recycling or the circular economy.

Almas Heshmati (2015) traces the first countries that introduced the concept of a circular economy at the state level. According to him, Germany is the first in this, since it started implementing the circular economy in 1996, although it had worked in this direction long before that. This act is accompanied by the entry into force of the Closed Cycle of Substances and the Waste Management Act. The law provides a framework for the implementation of closed-cycle waste management and provides environmentally compatible waste disposal and assimilative waste capacity. Another example of an attempt to start implementing the circular economy is in Japan. The Japanese government has developed a comprehensive legal framework for the country’s transition to a recycling-based society (METI, 2004; Moriya et al., 2005).

The Basic Law on the Establishment of a Recycling-Based Society, which came into force in 2002, provides quantitative targets for recycling and long-term dematerialisation of Japanese society (Van Berkel et al., 2009).

China is the third country which makes serious efforts to widely implement a circular economy. However, unlike in Germany and Japan, the Chinese government, for various reasons, such as maintaining competitiveness, initially introduced the framework of the circular economy on a smaller scale through a series of pilot studies so as to have a better basis for assessing its large scale and full coverage in the long run. This policy is similar to economic liberalisation, which began with economic free zones. Several other countries, such as Sweden, have long been consistently introducing various incentive programmes in an attempt to facilitate the optimal conditions for gradually and effectively increasing the rate of recycling through public education. The policy is successful and satisfies politicians and environmentalists (Heshmati et al., 2015).

When a business invests in value creation, long-term, sustainable and competitive economic value is achieved (Trifonova, 2019).

In the circular economy, production and consumption are increasingly based on the use of services instead on the possession of material goods. Companies are changing their operational models as well as updating their operations to support climate change mitigation (Sitra, 2019b).

The circular business model is an economic model in which consumption is based on the use of services - sharing, renting and recycling, instead of owning and producing more and more goods. In the end, the materials are not destroyed, but are used as a basis for new products and this process is repeated again and again (Sitra, 2019a).

The practical realisation of the circle in the economy happens through different business models. The Finnish innovation fund Sitra considers 5 business models (Fig. 1), namely: renewables; sharing platforms; product as a service; prolonging the life of the product; resource efficiency and recycling.
Product Life Extension - allows companies to extend product and asset lifecycle. The value that would otherwise be lost from worn-out materials is instead maintained or even improved through repair, renovation and recycling.

The product as a service - the manufacturer remains the owner of the product and provides only the service as an alternative to the traditional model of "buy and own". The products are used by one or more customers through a rental agreement or payment for use.

Resource efficiency and recycling (Circular supply) - provides fully renewable, recyclable or biodegradable resources, which are the basis of circular production and consumption systems by replacing raw materials with biological raw materials (renewable, recyclable and biodegradable) of ecodesign.

Utilisation of waste resources - allows companies to eliminate leakage of materials and maximise the economic value of product returns.

Sharing platforms - promotes platforms for cooperation and shared use of products between users - individuals or organisations.

Circular business models open up the value chain for new collaborations and services enabling bottom line impact (Fig. 2).

Business models from the circular economy in the raw material industry in Bulgaria

According to data from the Bulgarian Chamber of Mining and Geology in 2017, the total value of production of industrial enterprises in the mining industry amounted to BGN 2,85 billion (around 1,45 billion EURO), which is an increase compared to previous years.

The number of people employed in the mining industry in 2019 is 20,779 people, and the trend is insignificant compared to previous years.

The raw material industry is a specific one because the number of operating enterprises is relatively small, but they still manage to generate output and added value, which in absolute terms exceeds the production of many other industries.

The graph in Fig. 3 traces the pace of production since 2010, broken down by sub-sector. Each sub-sector has a relatively stable pace, as traditionally the highest productivity is in the sub-sectors “Mining of ore materials”, “Coal mining” and “Mining of industrial materials (non-metallic)”, as the total extraction of the raw and energy (coal) materials in our country in 2018 was in the amount of 108,42 million tonnes and there is a slight decrease compared to the previous year.
The examples of waste-free production in Bulgaria are becoming more and more, as the mining industry is among the leaders in the field of circular economy. For the sector, the situation is slightly different from the traditional one - material flows are usually large and concentrated and therefore the useful use of waste occurs much more often. Given the specifics of the activity, the business models that have been proven to be applicable are "Resource efficiency and recycling" and "Waste resource recovery".

An example in the circular economy is one of the best underground mines in the world - Dundee Precious Metals Chelopech. In 2005, the so-called chamber system was introduced with the subsequent filling of the seized mining spaces with hardening material, which includes all sterile rock masses and a large part of the flotation waste mixed with cement.

In Assarel Medet an oxide embankment (a hill formed by the disposal of oxide copper ores, once treated as waste) is simultaneously reclaimed and operated through a drainage system for catching and draining water to be directed to the production of cathode copper or treatment plants. Lavender is grown on the reclaimed land for oil production and honey is also extracted at the same time.

Survey results

At the beginning of 2020, in connection with INTERREG Europe project “REDUCES”, a survey was conducted among the companies from the Bulgarian mining industry, in order to establish the understanding and application of the models for circular economy. The survey was provided to 65 companies in the business, with only 13 of them participating in its completion.

The analysis of the results shows that in most of the surveyed companies circular models for modernisation and innovation are applied, namely:

- Opportunity for efficient processing of poor ores;
- Industrial water supply in a closed cycle to supply the production process;
- Mounting of an installation for extraction and electrowinning of cathode copper from mine water, through which an additional by-product is obtained - pure copper;
- Technology for extraction of accompanying gold in copper concentrate, so that precious components are not lost in the waste;
- Application of a method of extraction, which includes backfilling, i.e. the ground sterile rock mass is returned to the underground mine in the form of a pasty filling, is an example of a circular economy, which not only reduces the amount of waste deposited on the surface, but is also used the waste as a raw material, which is mixed with cement and returned to the seized chambers, ensuring the stability of the rock massif;
- Use of part of the mine ballast for filling the used spaces underground, for paving during the construction of the underground roads after crushing and for upgrading the walls of the tailings pond;
- In the extraction of limestone, necessary for the production of lime, many additional fractions of material are released, which are not discarded, but sifted and placed on the market for aggregates;
- Use of earth masses and sludge for reclamation of disturbed terrains;
- Delivery to specialised companies of used oils for recycling and use in other industries;
- Recycling of metals used for drilling tool crowns;

Fig. 3. Raw materials production by sub-sector, in thousand tonnes

![Production chart](chart.png)
Conclusion
The transition to a circular economy is determined by the argument that the linear model: extraction-production-consumption-waste is not sustainable because it requires continuous extraction of new raw materials.

In the context of the topic, Bulgaria lags behind, especially in terms of technologies for recycling and waste treatment. Knowledge is needed for fast and efficient use of technologies, as our country has the potential to introduce innovative waste policies.

The mineral resources industry, although poorly represented in the study, is prepared to meet the challenges of the concept and proves that it manages waste as a raw material.

Public policies, in the context of the EU's common policies in the field of the circular economy and the environment, are complex, difficult and multifaceted. All this requires going through many consultations and discussions, negotiations and legislative changes, as well as the engagement of a wide range of professional expertise. The state mechanism should be activated by stating its active state position and policy to strengthen the regulatory environment that favours the implementation of socially responsible practices, as well as the management of financial instruments for support.

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References
Bulgarian Chamber of Mining and Geology. 2010. Godishen byuletin 2010 – mineralny-surovinnata industriya v Bulgaria. BMKG, Sofia: https://www.bmgk.bg/%d0%b1%d1%8e%d0%bb%d0%b5%d1%82%d0%b8%d0%bd-%20%20%d0%b2/d1%80%d1%85%d0%b8%d0%b2/.


NON-DETONATING CHARGES IN POLYMER HOUSINGS FOR SMOOTH SPLITTING OF ROCK BLOCKS DURING PRIMARY EXTRACTION AND SECONDARY CUTTING

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ABSTRACT. In some cases, during the extraction of certain mineral resources, industrial explosives are not sufficiently safe for the environment in terms of generated shock waves, toxic gases, seismic waves, scattering and vibrations. The main reasons for these harmful effects of the explosion are the speed and the mechanism of the chemical reaction of explosive decomposition. The authors have focused their research on a variety of fast-combusting high-energetic compositions, that can fully replace the widely used detonating explosives in the extraction and secondary processing (cutting) of large stone blocks. Samples from polymer containers filled with non-detonating compositions, based on waste gunpowder and metal-containing pyrotechnic mixtures were subjected to field tests. The experiments were performed in real conditions on stone blocks with hardness f = 16 according to the Protodyakonov rock strength scale. Depending on the lengths of the blast holes, different charge designs were used.

Keywords: non-detonating blasting cartridges, propellants, smooth blasting, ornamental stone extraction

Introduction

The aims of the experiment are to develop ready-made charges, which during the extraction of rock cladding materials could fully replace industrial explosives and the expensive and risky blasting gunpowder (BGP). These devices should be resistant to external influences. Field tests with non-detonating charges in polymer containers are a new step in the study of the potential capabilities of low-speed energetic compositions for fulfilment of delicate blasting in the extraction of dimension stones. To achieve high economic and environmental efficiency of the products, the authors have focused their research on the creation of simplified production technologies and recipes with cheap and affordable raw materials. According with descriptions of Mitkov (2011), products from the dismantling of unnecessary ammunition were applied as a source of energy in the new generation mixtures.

Knowledge of the theoretical foundations of explosive influence in a solid medium, the differences between the action of high explosives and low-explosives, as well as the processes of crack formation in the rocks, plays a leading role in scientific and experimental activities.

Explosive impact in rock medium

As a result of the detonation of the explosives, a very high pressure of the gaseous products is obtained - up to hundreds of thousands of kilograms per square centimetre. Regarding Mitkov (2007), the explosive gases act on the walls of the explosion chamber. As a result, a shock wave (pressure wave) is generated in the rock. Under the action of that shock wave, two types of stresses arise at each point in the space around the charge: in the radial direction - compressive stresses, and in the tangential direction, parallel to the wave front - tensile stresses. As a result of the explosion, zones of crushing, breaking, cracking and concussion are formed in the rock (Fig. 1).

The radius of the crushed zone depends on the strength and elastic properties of the rock. It also depends on the mass and shape of the charge, as well as on the quality characteristics of the explosive, etc.

The fragmentation zone covers the system of circular and radial cracks in a perimeter of up to 100 radiuses of the charge.

Fig. 1. Blast induced influence in solid medium

The compressive and tensile stresses propagate behind the fragmentation zone, also. Their action is manifested in the displacement of the medium without disturbing its integrity. The action of the pressure wave is reminiscent of the action of seismic waves. This zone of oscillations and shocks covers a perimeter of 100 to 1000 radiuses of the charge (Fig. 2).

During the camouflet action of the explosion, the effects of the blast do not appear on the surface of the medium.
Concerning Mitkov (2010a), when blasting for destruction purpose, the charge should be positioned in such a way, that its action could reach the free surface. When the pressure wave reaches the open face, it reflects and spreads in the opposite direction as a tensile wave (Fig. 3). The tensile wave propagates towards the centre of the explosion, whereby the reflected wave is superimposed on the end of the falling wave. At a certain distance, the algebraic sum of the stress exceeds the tensile strength of the rock, as a result of which the particle detaches. The process is repeated until the difference between the tensile and compressive stresses exceeds the tensile strength limit. At a corresponding intensity of the initial parameters of the wave, the boundary of detachment from the surface comes to the charging chamber, forming a funnel.

The resulting shock waves are superimposed along the line between the boreholes, increasing the pressure forces generated in this plane (Fig. 6).

The compressive forces induce tensile forces in the shock waves, which act on the perpendicular plane to the direction of compressive shock (Fig. 7).

Fig. 6. Split crack formation as a result of generated tensile waves in the point of collision between two compressive shock waves

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The secret of successful cracking with high explosives is to blast high-speed explosives. The tensile strength of the rock is exceeded only in the area of shock waves accumulation, i.e. on the line between the holes.

Splitting with high explosives is not an easy task - if the specific consumption of the explosive is too high, cracking occurs not only along the desired line of separation, but in many random directions. At a lower specific consumption, the splitting is not obtained perfectly, and a large part of the energy of the gaseous products is dissipated in the surrounding rock in the form of cracks.

A serious problem (Fig. 1) in the deposits for rock cladding materials regarding the use of high-speed explosives is their distinctive “brizant” effect on the solid medium. The impact energy of their explosion pulverizes the rock immediately around the borehole - a zone of compression damage or the so-called "crushed zone". It is surrounded by a zone of instability of tension or the so-called “fragmentation zone”, where the pressure wave remains strong enough to cause a tensile force exceeding the tensile strength of the rock. Then, the created cracks are prolonged by the generated gas pressures. The intensity of the shock wave decreases with the travelled distance. The "seismic zone" begins where the stresses generated by the pressure wave cannot overcome the tensile strength of the material. Therefore, there is no cracking...
in this area - only vibrations. Sometimes, exactly these vibrations are able to cause an unexpected release of stress in the undisturbed rock environment at a great distance from the explosion. Such stress-release usually creates a crack with an unforeseen direction deep in the massif.

**Principle of operation of the propellants**

Regarding description of Boychev (2018), blasting gunpowder (BGP) is a deflagrating explosive, not a high explosive. The effect on the environment is a result of the pressure, caused by the retention of gaseous products from its combustion (Fig. 8).

![Fig. 8. Mechanism of splitting by blasting with propellants](image)

In practice, this is achieved by igniting the BGP in a suitably perforated and well-closed (plugged) blast hole. The explosive energy, generated by the compressed hot gases, causes the splitting due to overcoming of the tensile strength of the stone.

**Experimental part**

The observations on the behaviour of the explosive mixtures, packed in plastic housings, were carried out in real conditions of a quarry for extraction of rock blocks with monumental purpose.

**Studies of non-detonating compositions**

In selecting the appropriate formulations, the results of the laboratory tests of explosive mixtures published by Stoycheva and Shishkov (2019), were used as a starting point.

- **Mixture #1**: “flash-powder composition” 65% KClO₃ + 35% Al (dark) with Oxygen Balance = -1.12%;
- **Mixture #2**: 80% gridded DBP + 20% NH₄NO₃ prills with Oxygen Balance = -7.92%;
- **Mixture #3**: 70% gridded SB + 25% NH₄NO₃ + 5% Al (dark) with Oxygen Balance = -5.19%;

According to descriptions of Boychev and Asenov (2018), the sound-light pyrotechnic composition (Mixture #1) has high deflagration velocities in a closed space. It reaches a rate of 650 m/s with diameter of the charge 20 mm. When that mixture is sealed in a solid housing and the length of the charge is over 250 mm, it shows a tendency to pass from explosive combustion to detonation. This is not suitable for the purposes of the present experiment. To avoid adverse effects on the rock environment, containers with optimal dimensions, relative to the diameter of the blast holes (φ = 38 ± 45 mm), were chosen.

Compositions, based on waste smokeless gunpowder and ammonium nitrate (Mixture #2 and Mixture #3) have a lower bulk density and a lower rate of deflagration in closed space, compared to Mixture #1. But, theoretically, they emit about four times larger volume of gaseous products thereof. Ignited in the open space, these two mixtures burn with low speed of the order of 2-5 mm/s. Inserted in the selected hull, they cannot pass from deflagration to detonation. Also, they show a long period of increasing the rate of progressive combustion.

Actually, when propellant-based compositions are packed in a closed volume, due to the gaps between the coarser-grained ingredients and due to the porosity of the smokeless gunpowder, an enlarged combustion surface is formed. Conditions for the transition from layer-by-layer to convective combustion are created. Mitkov (2010b) reported, that as the pressure in the closed space increases, the speed of the process rises and passes to deflagration. This type of mixtures achieves explosive conversion speeds in the range of 250 to 530 m/s, when the diameter of the charge is up to 20 mm and the initial pulse is not powerful. If the density, the diameter, and the length of the charge increase, a transition of the process into atypical detonation could be expected, according to Boychev (2018). The reasons are the raising of pressure and temperature in the confined volume and the formation of shock wave. This phenomenon would cause additional fragmenting of the rock around the blast hole.

**Construction of explosive cartridges in polymer containers**

The main aim of the present research is to create ready charges from non-detonating compositions in a rigid waterproof package. The container has to protect reliably the reactive content from external influences. The polymer housing must ensure the initial course of the chemical reaction under conditions of confined space and high pressure, as it is written by Boychev and Assenov (2018). At the same time, the hull must prevent the transmission of an initiating pulse between the devices in one package and the escalation of accidental combustion into a mass explosion, according to information given by Mitkov (2010b). Activation of each “cartridge” should only be carried out by means of a built-in igniter.

For the needs of the experiment, the authors looked for options for a ready-to-use cheap plastic product that has a strong body with an inner diameter of about 20 mm and a length of about 150 mm. Its construction must allow easy and reliable airtight closure. The authors focused on the blanks for the production of bottles for carbonated drinks, with a screw cap closure. The so-called "Preforms" are made of durable polymeric material (polyethylene terephthalate) and have the necessary strength characteristics for our experiments (Fig. 9).

![Fig. 9. Construction of the plastic container for explosive charges](image)
Ten containers were filled with each of the prepared mixtures. The three types of compositions have different grain sizes of the components and therefore perform different bulk densities. Thus, the amount in a full container of Mixture #1 was 0.050 kg, of Mixture #2 was 0.030 kg, and of Mixture #3 was 0.032 kg. For ignition, ordinary electric igniters for pyrotechnic purposes with smooth burning of the fuse-head were chosen. The igniter was placed in the middle of the bulk charge. The electric wires were passed through a small hole in the screw cap, which was filled and sealed with hot silicone after closing the container. The ready samples were used for preparation of decoupled multi-deck chained charges - with air gaps in larger diameter blast holes.

Construction of the charges in the blast holes

Field tests of the prototypes were made in a quarry for extraction of stone blocks from magma rocks. The hardness coefficient of the rock was $f = 16$ according to Protodyakonov. To compare the effect of blasting of the three different mixtures, it was necessary to test them under approximately the same conditions. Rock formations with three open surfaces and a cleft-plane on the fourth side (or four open surfaces) were selected. Two parallel vertical blast holes with a length of 1.80 m and a diameter of $\varphi = 38 \pm 42$ mm were drilled in each of the three rocks. The distance between the two blast holes was not more than 0.60 m. So, the value of the compressive stresses in the collision zone between the two charges was sufficient to create perpendicular tensile stresses. Those tensile stresses should form a connecting crack between the holes. Under the influence of expanding gaseous products, this crack could propagate evenly to the free surfaces that are perpendicular to its plane.

Results and discussion

The use of chained charges without an intermediate stemming allows an even distribution of the explosive gas pressure along the entire length of the blast hole. Thus, the compressive stresses on the walls of the hole are the same and the chance of forming a crack in unwanted direction becomes smaller.

During the experimental splitting with the sound-light pyrotechnic composition Mixture #1 (Fig. 11) an excellent cracking of the rock body in the intended direction was observed. There was a significant displacement of the treated block, also. Due to the smaller diameter of the hulls, the charges do not have close contact with the walls of the blast hole and the air between them plays a buffer role by reducing the blasting effect on the rock. No parasitic cracks were observed on the detached surfaces.

Fig. 10. Configuration of the explosive charge inside the blast-hole

To determine the mass of the charge in an explosive hole, practical data, information from literature sources for calculating the parameters of smooth blasting and experimental results of past splitting with BGP at the same quarry were used. The weight of the charge in one linear meter of contour drilling was determined depending on the type of rocks and the characteristics of the explosive. Regarding data from Stoyanov (1994), when working in solid rocks with a hardness coefficient $f = 16$ according to Protodyakonov, a linear mass of up to 0.300 kg/m is accepted for industrial explosives with normal power. Under the same conditions, the so-called "Specific cost for the formation of one square meter of swath crack" is 0.500 kg/m$^2$, and the recommended distance between the contour blast holes with a small diameter is 0.5 - 0.6 m.

The authors decided to reduce the calculated linear mass of the charge by 50 to 70%, because, for the conditions of the current experiment, a smaller diameter of the blast holes was used and the aim was not smooth blasting, but to create a cut with walls protected from cracking. Thus, a linear mass of 0.150 kg/m was determined for Mixture #1, and 0.100 kg/m for Mixture #2 and Mixture #3, respectively. The calculated amount of charge from Mixture #1 was 0.270 kg for an explosive hole, and from Mixture #2 and Mixture #3 - 0.180 kg. The reason for this difference is theoretically the higher performance of the compositions that contain smokeless gunpowder.

Chained decoupled multi-deck charges of five explosive cartridges with the same content were placed in each blast hole (Fig. 10). They were completed by twisting the electric cables, leaving an air gap of 0.10 - 0.12 m between the containers. Thus, the total length of each ready "garland" was 1.30 m. After the chains were hung in the blast holes, thick paper plugs were placed and a reliable 0.60 m long inert stemming was built in. The wires of the five chained cartridges were connected in a parallel circuit. The electric blasting circuits from the two adjacent holes with equal charges were connected in parallel to the main cable. Three experimental blasts were carried out - each with the same construction of the charges, but from the respective explosive mixture.

Fig. 11. Experimental rock splitting by blasting with Mixture #1
In the experimental blasting with Mixture #2 (Fig. 12) a good crack of the rock body in the intended direction was observed, but with a slight displacement of the treated block. Immediately after the explosion, short bursts of flame were noticed through the newly formed crack in the rock. Due to the effect of progressive combustion of the smokeless gunpowder, the smaller diameter of the charges (related to the diameter of the blast hole) played a negative role on the acceleration of the chemical reaction in the volume of the individual charge. During the initial inflammation of the nearest particles of grinded gunpowder by the electric igniter, hot gases were released. That increased the pressure in the hull of the device and began to quicken the combustion process in the remaining volume of the composition. This, in turn, caused the plastic housing to open. So, the pressure dropped sharply. Until grains of the composition spilled into the wide volume of air spaces in the blast hole. As a result, attenuation of the deflagration and transition to low-speed combustion occurred. That’s why, a very low efficiency of the prototypes with Mixture #2 was shown, despite of the four times larger release of gaseous products compared to Mixture #1.

![Fig. 12. Experimental rock-splitting by blasting with Mixture #2](image)

The effect of the experimental blast with Mixture #3 (Fig. 13) was slightly better, but similar to that, described for Mixture #2. The added aluminium increased the temperature and rate of the explosive conversion. The higher velocity managed to react a bigger quantity of the charge. But, spillage of a mixture from destroyed hulls and decreasing pressure in the explosive chamber were observed here again. There was a smooth split, but insufficient expansion of the crack, as well as some residual flames.

![Fig. 13. Experimental rock-splitting by blasting with Mixture #1](image)

Conclusions

The results from the field tests of decoupled chained charges with Mixture #1 proved, that the optimisation of the technique for application of “flash-powder” pyrotechnic compositions, packed as ready charges in polymer housings is successful. Such non-detonating explosives can fully replace industrial explosives and blasting gunpowder (BGP) in the extraction and secondary processing of large stone blocks. The relatively high cost of the product is a disadvantage. It could be compensated by the reliefs in the mode of acquisition, transportation, storage and use which result from the lower hazard class of the products.

In terms of striving for lower costs, Mixture #2 and Mixture #3 contain the cheapest possible high-energy components - ammonium nitrate prills and secondary smokeless gunpowder. This gives a potential for high economic and environmental efficiency of the non-detonating explosive cartridges. The generation of several times larger volume of gaseous products from these two mixtures, compared to Mixture #1 and BGP, guarantees significantly better performance of their charges in case of high deflagration rates. Owing to good performance, the relative cost of explosives can be reduced, and this will contribute to even higher economic efficiency of blasting. The results of the in-situ blasts show that additional research and field tests are needed to increase the efficiency of these charges. The authors are planning to continue their research in two directions:

- testing of the current construction of the products in conditions of multi-deck charges with an intermediate inert stemming of dry sand, which will seal the space around the cartridges and prevent spillage of the composition and decreasing of pressure;
- designing of changes in the construction, to increase the strength of the initial ignition pulse and to enlarge the initial area of combustion inside the charge.

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References


Mitkov, V., 2011. Razrabotvane i izsledvane na novi zariadi ot utilizirani boepripari. Geology and mineral resources, 4, 30–33. (in Bulgarian).

Mitkov V., 2010a. Bezopasnost pri proizvodstvoto i upotrebata na eksplozivi. (in Bulgarian).


Stoyanov D., 1994. Rakovodstvo za uprazhneniya po probivno-vzrivni raboti v otkriti rudnici, karieri i stroitelstvoto”, MGU, Sofia. (in Bulgarian)

Stoycheva N., Shishkov P., 2019. Innovative formulations for a new generation of low-speed explosive compositions, designed for blasting in tender conditions and for extraction of rock-cladding materials. Journal of Mining and Geological Sciences, 62(2), 94–99. (in English)
DETECTION AND MONITORING OF MANGANESE IN DRINKING WATER AND GROUNDWATER THROUGH PHOTO-OXIDATION SENSORY REACTION WITH ULTRA-SMALL CARBON NANODOTS

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ABSTRACT. The paper focuses on the development of ultra-small carbon nanodots as sensitive sensors for detection and monitoring of manganese in drinking water and groundwater. The environmental contamination with manganese is often a result from industrial activities such as mining and agriculture. The soluble Mn ions are toxic for many organisms and might even cause serious human diseases. The strategy for sensory detection used by us is based on a photo-oxidation reaction, in which the carbon nanodots are dissolved in acidic solution and illuminated with UV irradiation (λ = 365 nm). At these conditions the nanoparticles acted as photosensitizer and produced singlet oxygen, which can be monitored by 3,3’,5,5’-tetramethylbenzidine as an organic indicator. However, to proceed this reaction, it is necessary to introduce the redox pair Mn(II)/Mn(III) in the reaction mixture, which plays the role of a catalytic mediator for the electron transfer. Thus, the oxidation of 3,3’,5,5’-tetramethylbenzidine appears, which results in blue colour of the solution with absorbance maximum at 645 nm. The rate of this sensory reaction was significantly enhanced in the presence of EDTA, which was used as a ligand to obtain a stable complex of Mn(III)/EDTA. The formed complex itself oxidised the organic indicator and caused the colorimetric reaction. Among the other metal ions tested, only manganese could be detected by the presented sensory approach.

Keywords: manganese detection and monitoring, ultra-small carbon nanodots, sensory reaction

Introduction

Manganese (Mn) is one of the most abundant metals found in the earth’s crust (Chiswell and Huang, 2006). The groundwater percolating through rocks and soil can dissolve various minerals containing Mn (Khadse et al., 2015). In nature, Mn exists mainly in its oxidised chemical forms Mn2+ and Mn3+ (Armstrong 2008). For example, in aquifers where the amount of dissolved oxygen is low, higher levels of dissolved Mn2+ can be found (Zhang et al., 2020). Thus, the highest concentrations of manganese are measured in groundwater, which is a rare phenomenon for the surface water (Dieter et al., 1992). In most studies elevated Mn in groundwater is due to bedrock leaching, but in other cases the pollution can be caused by industrial activities, such as mining, dump sites and agriculture (Wuana and Okeime, 2011). The overexposure to this transition metal might be toxic to many organisms and their different life stages (O’Neal and Zheng, 2015). Several studies have demonstrated the negative association between elevated Mn in drinking water and the caused human diseases (Vollet et al., 2017).

The atomic absorption spectrophotometric analysis is one of the most widely used chemical methods for monitoring of Mn in the contaminated environment (Bulska and Ruszczyckis, 2017). However, the colorimetric, fluorometric and plasma atomic emission analytical techniques are also recommended for measuring Mn in environmental samples. Inductively coupled plasma (ICP) atomic emission analysis is frequently employed for determination of the total Mn amount, but it cannot distinguish the different oxidation states of manganese (Wilschefski and Baxter, 2019). Although each of these methods is known for its extremely high precision, there are certain drawbacks that make them difficult to access for massive use, particularly in the developing countries. The main obstacle is that their price is too high, i.e. they require huge investments, expensive maintenance, as well as highly qualified staff (Park et al., 2018). In addition, the samples preparation often involves use of numerous aggressive and toxic reagents, complicated chemical protocols, and diverse approaches or procedures, which might destruct the environmental sample (Bamforth et al., 2006).

In the last decade the carbon nanodots (C-dots) have been developed as promising and environmentally friendly nanomaterials for biosensing and metal ion detection (Tuerhong et al., 2017). For example, fluorescent C-dots were already utilised for detection of Hg2+, Ag+, Fe2+, Fe3+ and Ca2+ (Loukanov et al., 2018). In all methods the C-dots are prepared by economical and green chemical approach, which makes them appropriate for mass usage in simple analyses instead of the classical expensive analytical techniques. The use of C-dots requires also simple synthesis and sample preparation, common analytical tools as absorbance and fluorescence spectrophotometers.

The purpose of the currently reported work is to develop the carbon nanodots as nanosensors for detection and monitoring of Mn in drinking water and groundwater. For that purpose the photo oxidation properties of C-dots were investigated under irradiation with 365 nm UV light. Under these conditions the C-dots acted as photosensitisers and generated singlet oxygen (1O2). The process is pH dependent and the presence of singlet oxygen can be monitored by oxidation of an organic indicator as 3,3’,5,5’-tetramethylbenzidine (TMB). However, in aqueous solution the migration of 1O2 is very short and the deactivation to its triplet state is occurring very fast. So, to proceed with the process of photo oxidation it is necessary to have the cooperation of a mediator that might enhance the efficiency of electron transfer. Manganese was chosen as an appropriate candidate for this role, because Mn3+ possesses strong oxidation power. This was the key step in our investigation toward development of nanosensor for manganese. The adding of Mn2+ to the aqueous solution significantly enhanced the oxidation of TMB. This process occurred with very high efficiency at slightly acid
pH of the reaction mixture. In case of other metals this effect was not observed. Only Mn^{2+} demonstrated such enhancement of the photo oxidation reaction, and therefore our efforts were concentrated to develop this reaction as a sensory process.

**Experimental Procedures**

**Materials and analytical instrumentation**

All chemicals used in the protocols below were of analytical-reagent grade. Sodium acetate (\(\text{CH}_3\text{COONa}\)), citric acid (\(\text{C}_6\text{H}_5\text{O}_7\)), ethylenediaminetetraacetic acid disodium salt (\(\text{Na}_2\text{H}_2\text{N}_2\text{O}_8\)), EDTA, ethylenediamine (EDA) and all metal chloride salts were purchased from WAKO. 3,3’,5,5’-Tetramethylbenzidine (TMB) was purchased from Sigma Aldrich and dissolved in dimethylsulfoxide (DMSO) to generate a freshly prepared stock solution. UV-VIS spectroscopy was performed on UV-VIS Jasco analytical spectrophotometer (model No V-570) using 1 cm quartz cuvette. The UV-VIS absorption spectra were taken of C-dots (5 µg/mL), Mn(III)-EDTA (10 mM Mn(II)), 20 mM EDTA) and oxidised TMB (0.8 mM, pH 3.5-7.5). The nanoparticle emission was quantitatively measured by photoluminescence spectrophotometer (Jasco analytical photoluminescence UV-VIS, model No FP-6300).

The fluorescence lifetime of C-dots with different concentration of manganese were measured on a Fluorolog-3 spectrophotometer with a DeltaDiode (370 nm excitation) as the excitation source and a picosecond photon detection module as the detector. The phosphorescence spectra of the emission source and a picos...
Results and discussion

The irradiated with UV light ($\lambda = 365$ nm) C-dots are able to convert the oxygen molecule from triplet state ($^3$O$_2$) to singlet electronic state ($^1$O$_2$) as shown in the photochemical reaction (Fig. 1A). Because of differences in their electron shells, the singlet oxygen is much more reactive in comparison to the triplet oxygen. It is pH-dependent (usually pH < 4.5) and as a result the TMB is oxidised and the reaction solution colour turns to blue. Without manganese as a catalyst, the UV irradiation alone cannot oxidise TMB. Manganese is a good candidate as a mediator, because the Mn$^{3+}$ ion from the redox pair Mn(II)/Mn(III) has strong oxidation power, stability and significantly enhances the efficiency of the electron transfer. The reaction can be significantly improved in the presence of EDTA. We have assumed that the aqueous Mn(II) can be stabilised by these ligands, i.e. the formation of Mn(III) EDTA complex. Without EDTA the reaction of photo-oxidation occurred only in acidic pH condition. Nevertheless, if EDTA is added TMB can be oxidised even at neutral pH. The reason that this reaction proceeds under the UV illumination is that the C-dots absorption peak is located around 350 – 360 nm (Fig. 1B). After illumination with 365 nm light, an absorption peak at 645 nm emerged (Fig. 1C) and the reaction solution turned to blue. The stability of Mn(III)/EDTA complex enables the aqueous Mn(II) can be oxidized in the presence of EDTA or UV this delayed reaction of post oxidation can be separated from the oxidation reaction. This was observed when TMB was added 5 min after turning off the UV-lamp. Because the solution still contained Mn(III)/EDTA complex at that time, the oxidation of TMB occurred instantaneously. Therefore, without the presence of EDTA or UV this delayed reaction of post oxidation did not occur. Thus, the role of generated Mn(III) and its stability was confirmed. In our experimental setup the C-dots acted as a nanosensor photosensitizer and the presence of detected manganese did not quench their fluorescence at 480 nm. The sensory reaction proceeded because Mn(II) can be oxidized to Mn(III) by the dissolved oxygen, but the rate of this reaction normally is too slow. So, the results in our experiment suggested that the generation of oxygen in singlet state was responsible for the oxidation of Mn(II). In order to confirm this hypothesis we analysed the phosphorescence emission of 1O$_2$ at 1725 nm (as shown on Fig. 2A). By this analytical method it is possible to observe directly the red glow of the sample due to the singlet oxygen contents. As shown, the emission possesses high intensity phosphorescence peak (above 4000 a.u.). If Mn(II) was added into a solution of C-dots in CD$_3$CN – D$_2$O mixed solvent ($\nu/\nu$ = 15 /1) the intensity decreased by about 40-45 %. However, if EDTA is added too, the phosphorescence of singlet oxygen completely disappeared. Therefore, the role of Mn(II) is not to produce any peroxides but just to oxidise and form Mn(III), which is a strong oxidant and reacts with TMB as shown on the equation (Fig. 1A). Taken together Mn(II)/Mn(III) act as a catalytic mediator, which is the main reason for the unique sensory reaction. To test this observation we tried an assay of nine other metals (Ni$^{2+}$, Pb$^{2+}$, Fe$^{3+}$, Cr$^{3+}$, Co$^{2+}$, Hg$^{2+}$, Cu$^{2+}$, Zn$^{2+}$), which are known as common pollutants of the environment. As shown on Fig. 2B, among them only Mn$^{3+}$ ion is characterised with the ability to oxidise TMB. Some other metals can also form redox pair (2+/3+), for example Co(II)/Co(III) or Fe(II)/Fe(III) but they are not powerful enough to oxidise TMB and change the colour of the reaction solution into blue. Although cobalt is also a strong oxidiser, the form of Co(III) is unstable at these conditions or it does not react with TMB. The absorption spectrum of all these metals even in the presence of EDTA did not change significantly the absorbance at 645 nm when irradiated with UV light.

![Fig. 2. (A) Phosphorescence spectra of singlet oxygen ($^1$O$_2$) induced by the irradiated C-dots in CD$_3$CN – D$_2$O mixed solvent. (B) Test of metal cations with concentration 1 mM to oxidise TMB in the presence of EDTA (1 mM) and under illumination with UV light $\mu = 365$ nm. The absorbance intensity was measured at 645 nm. Among tested metals only manganese has an ability for enhanced oxidation. (C) Data from DLS analyses. (D) TEM micrograph of the synthesized C-dots](image-url)
As mentioned above the ultra-small C-dots act as photosensitizer nanosensor for the detection and monitoring reactions of manganese. Their size distribution was revealed by combining dynamic light scattering (DLS) and transmission electron microscopic (TEM) observation. DLS analysis (Fig. 2C) demonstrated that the nanoparticle hydrodynamic diameter is distributed in the range of 2 – 6 nm with an average value of 3 nm. These data were supported by TEM observation and measurement (Fig. 2D). C-dots appear on the micrograph as nanoparticles, which are uniform in size. Their shape is spherical. From the TEM image, only the bigger nanoparticles (diameter > 3 nm), which have higher contrast from the background granularity of the carbon film, could be distinguished. And even so, sometimes it is challenging to distinguish the right location and the outlines of the low contrasted nanoparticles, because the imaging of predominantly carbon structures on carbon grids does not allow the precise determination of the objects.

**Conclusion**

We have developed ultra-small carbon nanodots as nanosensors for detection and monitoring of manganese in water. The specificity of sensory reaction is based on the unique properties of Mn(II) ions to catalyse and enhance the oxidation rate of TMB in the presence of singlet oxygen produced via photosensitisation of illuminated C-dots with UV light. The photo-oxidation induced reaction is effective in acidic pH and the presence of EDTA used as ligand for Mn(III)/EDTA complex formation. The reported protocol for sample preparation and analytical data can be used for selective and sensitive detection of manganese in contaminated environmental samples, including environmental impact assessment.

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**References**


