SUSTAINABLE EXTRACTION AND PROCESSING OF RAW MATERIALS

Edited by Prof. Dr. Marinela Panayotova

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Dear readers and authors,

It is a great honour for me to present to your attention the third volume of the "Sustainable Extraction and Processing of Raw Materials" Journal (SEPRM) published by the University of Mining and Geology "St. Ivan Rilski", Sofia, Bulgaria.

The "Sustainable Extraction and Processing of Raw Materials" Journal is 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 of our society. 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 (comminution, milling and dewatering), physicochemical separation methods (flotation, bio-, hydro-, and electrometallurgy), 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 acknowledge the contribution of all the prominent scientists who agreed to be members of the SEPRM Editorial board!

I am grateful to all authors who have chosen SEPRM Journal to share their research!

I am happy to announce that the previous volume of the SEPRM is indexed in Google Scholar and included in BASE, OpenAIRE, Academic Resource Index (ResearchBib), ROAD, the Russian Scientific Electronic Library (eLIBRARY) and the National Reference List of Contemporary Bulgarian Scientific Publications with Scientific Review. It is archived in COBISS and in the Bulgarian Portal for Open Science certified according to CoreTrustSeal standards and Bulgarian National Library.

Editor-in-Chief: Prof. Dr. Marinela Panayotova
GRATITUDE TO REVIEWERS

I would like to express my deep thankfulness to all reviewers for their time and dedicated labour to review all papers submitted to the SEPRM Journal in order to choose the soundest works.

All members of the Editorial board, except those who are co-authors in this volume, served as reviewers.

This volume of the journal is available also due to the efforts of the volunteer reviewers - colleagues listed below:

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Dear Colleagues,

I am very obliged and thankful to you!

With a hope for further cooperation,

Yours Sincerely,

M. Panayotova, Prof. Dr., Editor-in-Chief - SEPRM Journal

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MINERALOGICAL AND HYDRAULIC CHARACTERISATION OF HISTORIC FLOTATION TAILINGS

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ABSTRACT. A composite flotation tailings sample from historic Medet tailings dam was characterised to understand occurrences of copper and hydraulic properties of the material and to determine if there is an economic benefit of its reprocessing using hydrometallurgical processes. Conventional ICP-OES multi-element scan and carbon and sulphur determination by Leco were followed by sequential copper assay and mineralogical analysis using the Tescan Integrated Mineral Analyser (TIMA) to identify the elemental composition, acid soluble copper and mineral abundance and liberation. The tailings sample contained 0.105% Cu, 0.41 % S and 0.05% C. The analysis of the gangue minerals showed that the bulk of the material is made up of plagioclase feldspar with moderate amounts of K-feldspars and small amounts of mica, chlorite and clay minerals. Copper minerals cuprite and chalcopyrite with minor amounts of covellite and bomite were observed in the mineralogical analysis of the sample by TIMA. Based on the sequential copper assays, it was estimated that approximately 59.8% of copper contained in the sample reports as acid soluble copper. To understand the flow behaviour in the material the main hydraulic properties like hydraulic conductivity and moisture retention capacity were determined.

Key words: tailings, copper, minerals, hydraulic properties

Introduction

Waste materials generated during flotation processing of finely ground ore and stored in the historical tailings storage facilities generally contain significant amounts of metals of interest. This is mainly due to some inefficiencies in the existing beneficiation techniques at the time of active operations. However, as primary ores are increasingly degrading and becoming more complex, historical flotation tailings are more frequently regarded as an important alternative source of various metals (Grigorova, 2011; Shengo and Maloba, 2013; Grigorova et al., 2015; Stanković et al., 2018; Babel et al., 2018; Figueiredo et al., 2019; Yankova, 2020).

The Medet Tailings Dam contains copper flotation tailings, generated by the Medet and Assarel operations from 1965 until 1990. It is located near the town of Pirdop in the Sredna Gora Mountain and accommodates approximately 170 million tones of waste material as reported by Sultanov (2001). This study examines if hydrometallurgical reprocessing of the Medet Tailings Dam materials could enable viable copper recovery.

The specific study objectives were to: (1) define physical properties of the materials, like bulk and particle density, particle size and screen characteristics; (2) determine the total copper content and the content of other elements, as well as the overall mineral abundance, copper bearing mineral associations and acid consuming gangue minerals (3) assess leachability of copper in the deposited material and (4) characterise the material hydraulically by saturated hydraulic conductivity and moisture retention determinations. The results from this study were used as a first step in the assessment whether the leaching processes are technically feasible for tailings reprocessing of the Medet Tailings Dam.

Materials and Methods

Sampling

The tailings material with a total weight of approximately 320 kg was sampled from thirteen (13) pits excavated in pre-selected areas of the tailings dam, as given in Figure 1. Thirteen (13) samples were collected from the pit depth greater than 3 meters to reject the sampling of upper layers material with very low (0.03%) copper content. The samples were designated with the letters from A to M.

Fig. 1. Image of the Medet Tailings Dam with the location of sampling points

A composite sample identified as a MT-H was prepared so that each pit sample is properly represented in one overall sample representing the total material collected. The MT-H sub-samples were submitted to Process Mineralogical Consulting Ltd. for elemental and mineral analysis and to GeoSystems Analysis Inc. for hydraulic characterisation.

Sample characterisation

The tailings samples were characterised physically, chemically and mineralogically. These studies included specific gravity and bulk density determination, size analysis, chemical and mineralogical analyses and sequential copper assay.

The bulk density of the material was measured with 100 ml cylindrical vessel of stainless steel and the particle density was determined by the use of water pycnometer. A combined sieve and hydrometer analysis was used to determine the particle size distribution of the tailings material. The elemental analysis was performed by Inductively-Coupled Plasma Optical Emission Spectroscopy (ICP-OES) multi-element scan, whereas carbon and sulphur were separately analysed with the Leco carbon-sulphur analyser. To identify the mineral abundance, type of the copper bearing minerals, liberation and association, nine (9) polished sections were prepared and each polished section was analysed utilising the Tescan
Integrated Mineral Analyser (TIMA) equipped with widely used scanning electron microscope (Dobrev et al., 2009; Valchanova et al., 2011; Schulz et al., 2020). The amounts of oxide minerals, secondary sulphide minerals, and primary copper minerals were determined using semi-quantitative diagnostic technique, referred as sequential copper assay. The leaching procedure used for the assay was as outlined by Parkinson and Bhappu (1995).

The saturated hydraulic conductivity of the material was determined utilising the standard test method (ASTM D 2434-68, 2006) and the moisture retention characteristic curve was determined using pressure plate extractor (ASTM D6836-16, 2016). A one-dimensional (1-D) consolidation test was performed by GeoSystems Analysis Inc. to determine compression, porosity and estimated height of the tailings material when subjected to an increased loading.

**Results and Discussion**

**Bulk Density and Specific Gravity**

The bulk and particle density of the tailings sample were determined as 1.54 g/cm³ and 2.74 g/cm³, respectively.

**Size Analysis**

The combined sieve and hydrometer analysis on the MT-H sample was conducted by GeoSystems Analysis Inc. to assess the particle size distribution of the material. The P₉₀ and P₅₀ for the MT-H sample were determined to be 0.3 mm and 0.05 mm, respectively. The results are presented in Figure 2.

![Particle Size Distribution](image)

**Chemical Analysis**

The chemical analysis of the tailings material was performed by Process Mineralogical Consulting Ltd. The assayed copper content was 0.105% and the value is consistent with the previous available data, published by Sultanov (2001). The tailings also contained 0.41% S and 0.05% C. The results from ICP-OES and Leco analyses are provided in Table 1. As can be seen from Table 1, the major elements include Al, Ca, Fe, K, Mg and Na and minor elements include Ti. The tailings also contain Ba, Cr, Mn, P, Sr and V with concentrations above 100 ppm, and trace elements Mo, Ni and Zn.

<table>
<thead>
<tr>
<th>Table 1. Chemical analysis of flotation tailings material</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Parameter</strong></td>
</tr>
<tr>
<td>Cu</td>
</tr>
<tr>
<td>S</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>Ag</td>
</tr>
<tr>
<td>Al</td>
</tr>
<tr>
<td>As</td>
</tr>
<tr>
<td>Ba</td>
</tr>
<tr>
<td>Be</td>
</tr>
<tr>
<td>Bi</td>
</tr>
<tr>
<td>Ca</td>
</tr>
<tr>
<td>Cd</td>
</tr>
<tr>
<td>Co</td>
</tr>
<tr>
<td>Cr</td>
</tr>
<tr>
<td>Fe</td>
</tr>
<tr>
<td>K</td>
</tr>
<tr>
<td>La</td>
</tr>
<tr>
<td>Mg</td>
</tr>
<tr>
<td>Mn</td>
</tr>
<tr>
<td>Mo</td>
</tr>
<tr>
<td>Na</td>
</tr>
<tr>
<td>Ni</td>
</tr>
<tr>
<td>P</td>
</tr>
<tr>
<td>Pb</td>
</tr>
<tr>
<td>Sb</td>
</tr>
<tr>
<td>Sr</td>
</tr>
<tr>
<td>Ti</td>
</tr>
<tr>
<td>Tl</td>
</tr>
<tr>
<td>V</td>
</tr>
<tr>
<td>W</td>
</tr>
<tr>
<td>Zn</td>
</tr>
</tbody>
</table>

**Mineralogical Analysis**

The prepared polished sections were scanned using TIMA technique by Process Mineralogical Consulting Ltd. to identify the mineral abundance. The resulting mineral list is provided in Table 2 along with the values regarding the abundance of each material.

<table>
<thead>
<tr>
<th>Table 2. Minerals identified in flotation tailings material</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mineral</strong></td>
</tr>
<tr>
<td>Pyrite</td>
</tr>
<tr>
<td>Chalcopyrite</td>
</tr>
<tr>
<td>Bornite</td>
</tr>
<tr>
<td>Tetrahedrite</td>
</tr>
<tr>
<td>Chalcocite</td>
</tr>
<tr>
<td>Covellite</td>
</tr>
<tr>
<td>Chrysocolla</td>
</tr>
<tr>
<td>Malachite</td>
</tr>
<tr>
<td>Cuprite</td>
</tr>
<tr>
<td>Cu-Sulfate</td>
</tr>
<tr>
<td>Other Cu</td>
</tr>
<tr>
<td>Oxides</td>
</tr>
<tr>
<td>Quartz/Feldspar</td>
</tr>
<tr>
<td>K-Feldspar</td>
</tr>
<tr>
<td>Mica</td>
</tr>
<tr>
<td>Clay minerals</td>
</tr>
<tr>
<td>Chlorite</td>
</tr>
</tbody>
</table>
The mineralogical analysis of the material provided a detailed analysis of the gangue minerals present in the sample and showed that much of the material is made up of quartz/feldspar (61.2%), moderate amounts of K-feldspar (20.7%), with lesser amounts of mica (7.84%) and chlorite (4.33%), and minor amounts of clay minerals (1.33%). In addition to the gangue mineralogy, the TIMA results revealed copper distribution by mineral species according to Table 3.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonates</td>
<td>%</td>
<td>0.30</td>
</tr>
<tr>
<td>Apatite</td>
<td>%</td>
<td>0.41</td>
</tr>
<tr>
<td>Other Silicates</td>
<td>%</td>
<td>1.46</td>
</tr>
<tr>
<td>Other minerals</td>
<td>%</td>
<td>0.55</td>
</tr>
<tr>
<td>Unclassified</td>
<td>%</td>
<td>0.01</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>%</td>
<td>100</td>
</tr>
</tbody>
</table>

The liberation characterization based on the exposed surface area is presented in Table 4, where copper sulphides and oxides are grouped as suggested by Tonžetić (2015) into three categories: “60-100%”, “20-60%” and “<20%”.

<table>
<thead>
<tr>
<th>Copper mineral groups and liberation category</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu Sulfide 60-100%</td>
<td>%</td>
<td>8.2</td>
</tr>
<tr>
<td>Cu Sulfide 20-60%</td>
<td>%</td>
<td>14.9</td>
</tr>
<tr>
<td>Cu Sulfide &lt;20%</td>
<td>%</td>
<td>36.2</td>
</tr>
<tr>
<td>Cu Oxide 60-100%</td>
<td>%</td>
<td>23.2</td>
</tr>
<tr>
<td>Cu Oxide 20-60%</td>
<td>%</td>
<td>14.5</td>
</tr>
<tr>
<td>Cu Oxide &lt;20%</td>
<td>%</td>
<td>4.90</td>
</tr>
</tbody>
</table>

As can be seen from Table 4, the distribution of copper based upon the exposed surface area shows that 21.1% of the copper as sulphides and around 37.7% of the copper as oxides can be classified as “liberated” and “middlings”. In aggregate, copper exposed to leach solutions and available to in-situ po

Sequential Copper Assay

The stages of sequential copper assay were chosen based on the results from the mineralogical analysis provided in the previous section. The results of the sequential copper assay and calculated total copper are provided in Table 5.
An estimation of copper minerals based on the sequential leaching are presented in Table 6.

### Table 5. Sequential copper assay results

<table>
<thead>
<tr>
<th>Leach Stage</th>
<th>Copper (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic Acid Leach</td>
<td>0.05</td>
</tr>
<tr>
<td>Sulphuric Acid Leach</td>
<td>0.01</td>
</tr>
<tr>
<td>Cyanide Leach</td>
<td>0.02</td>
</tr>
<tr>
<td>Four-Acid Digestion</td>
<td>0.02</td>
</tr>
<tr>
<td><strong>Total Copper, calculated</strong></td>
<td><strong>0.10</strong></td>
</tr>
</tbody>
</table>

The results from the 1-D consolidation test are summarised in Table 7.

### Table 7. 1-D consolidation test results

<table>
<thead>
<tr>
<th>Loading (pcf)</th>
<th>Compression (%)</th>
<th>Porosity (cm$^3$/cm$^3$)</th>
<th>Estimated tailings height (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>0.485</td>
<td>0.3</td>
</tr>
<tr>
<td>1000</td>
<td>0.92</td>
<td>0.480</td>
<td>2.5</td>
</tr>
<tr>
<td>5000</td>
<td>2.2</td>
<td>0.473</td>
<td>12.6</td>
</tr>
<tr>
<td>10000</td>
<td>3.7</td>
<td>0.465</td>
<td>24.9</td>
</tr>
</tbody>
</table>

The results from the sequential copper assay show that 49.5% of the copper is in copper oxides, 10.3% is in chalcocite, 20.6% is in secondary sulphides and 19.6 is in chalcopyrite.

As determined by sequential copper assays, approximately 59.8% of the copper contained in the samples is reported as acid soluble copper and it could be leached relatively easy.

### Hydraulic Characterisation

To evaluate if the tailings material is suitable for leaching, the main hydraulic properties - like saturated hydraulic conductivity, compression and moisture retention capacity were determined by GeoSystems Analysis Inc., using modified methods, originally developed for agricultural and engineered soils.

The saturated hydraulic conductivity ($K_{sat}$) of the material was found to be 1.5 x 10$^{-5}$ cm/s. The value is consistent with those measured in similar tailings storage facilities (Aubertin et al, 2011, Adajar and Zarco, 2014). Based on the obtained $K_{sat}$ results, the material has a mixed textural structure (clay loam, sandy clay loam or silty clay loam) and belongs to the moderate low permeability class.

Fig. 5. Copper distribution by copper species and exposed surface area of particle (TIMA image)

Fig. 6. MRC curves (An unnamed SWRC software image)
texture water holding characteristics and similar to fine sand. The Moisture Retention Characteristic data could be used further to predict the flow behaviour and to quantify the leach solution that should be applied to fully contact the material.

Conclusions

A detailed mineralogical and hydraulic characterisation of the flotation tailings from historic Medet tailings dam were carried out to obtain data for further assessment and selection of the most efficient type of the leaching process for copper recovery. The most significant outcomes from the study are as follows:

- The assayed copper content of the tailings material is 0.105%. Copper content in the upper layers (3-3.5 m) of the tailings dam is 0.03% in average;
- With P_{95} of around 250 μm the material could be classified as fine grained;
- Copper is mainly present as cuprite (~43%) and chalcocpite (~43%) with minor amounts of covellite (8.82%) and bornite (4.56%) and trace amounts of malachite (0.19%), chrysocolla (0.19%), chalcocite (0.10%) and tetrahedrite (0.07%);
- Given the amount of cuprite and other secondary copper minerals along with potential accessibility of leaching solution through grain boundary pathways and results from sequential copper assays, the tailings material indicates good leachability;
- With saturated hydraulic conductivity (K_{sat}) of 1.5 x 10^{-5} cm/s, the material has moderate to low permeability.

The successful application of a leaching process on the tailings material will depend mainly on the overall mineral abundance, mineral liberation characteristics, permeability and the amount of the small particle size fractions.

Further extensive and well planned metallurgical testwork to define copper extraction and acid consumption is required before the final decision on project feasibility.

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Stanković V., Milosevic V., Milicicic D., Gorgievski M., Bogdanovic G., 2018. Reprocessing of the old flotation tailings deposited on the RTB Bor tailings pond - a case study, Chemical Industry and Chemical Engineering Quarterly, 24 (4), 333-344.
CARBON NANODOTS AS LIGHT-ACTIVATED OXIDASE NANOZYME FOR ECO-FRIENDLY LEACHING OF COPPER FROM SCRAP

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ABSTRACT. The copper is the second largest strategic raw material. Since there is a huge gap between copper production and consumption, a green and eco-sustainable recycling technology is necessary that is able to process the copper from secondary sources of waste and scraps. Here we demonstrate the photo-oxidising properties of pyrrolic nitrogen-dominated carbon nanodots as eco-friendly and powerful oxidase-mimicking nanozyme for leaching of copper from metal scrap under irradiation with either ultraviolet or natural sun light (average intensity of 59 000 lx). The ultra-small nanoparticles with diameter < 5 nm were prepared by 600 W microwave-assisted pyrolysis, which might be considered as energy efficient synthetic method. The developed strategy enables to dissolve Cu metal at neutral pH range (between 5.1 – 8.3) and it might break the pH limitation for recycling of copper in the conventional chemical methods, where toxic and corrosive substances are used. The obtained yield was about 5 %, which is still not satisfactory for practical application in recycle technology. Nevertheless, according to our knowledge there is not any other reported photosensitizer nanozyme, which is capable to induce oxidation and dissolving of copper under natural light irradiation of neutral leaching solution.

Key words: oxidase-mimicking nanozyme, carbon nanodots, copper leaching

Introduction

The functional nanomaterials with enzyme-mimicking properties, also known as “artificial enzymes” or nanozymes, are a stimulating branch of biomimetics, which have attracted considerable attention due to their potential application as alternative catalysts of natural enzymes (Zhang et al., 2021). Among them the carbon-based nanomaterials have generated enormous scientific excitement because of the higher stability and lower cost than those of protein enzymes (Wang et al., 2021). Other reasons are also the diversified structural modulations and opportunity to be used as a platform for passivation, chemical modification and bioconjugation, as well as the absence of metal atoms or ions in their chemical contents (Jin et al., 2021). In that respect, the ultra-small pyrrolic nitrogen-dominated carbon nanodots (C-dots) were found to perform an efficient both peroxidase and oxidase-mimicking activity (Loukanov et al., 2022), which can be modulated by either pre-engineering of their surface structures or introducing a photo-regulated host-guest reaction (Lv et al., 2018). These metal-free materials are quasi-spherical nanoparticles that comprise amorphous nanocrystalline cores with a diameter between 1 – 5 nm (Wei et al., 2020). The oxidase-mimicking properties of nitrogen-doped C-dots have been systematically investigated under ultraviolet and visible (UV-Vis) irradiation and the nanoparticles were proved to exhibit catalytic ability close to that of their natural counterpart (Garg and Bisht, 2016). Therefore, the ultra-small C-dots can be classified as light-activated oxidase nanozymes (Loukanov et al., 2022). In fact, during the photo-catalytic process, reactive oxygen species are generated (Lv et al., 2018). C-dots catalytic activity is irrelevant to any cation-related binding sites and many references report that the nanozyme is able to produce reactive singlet oxygen (Zhang et al., 2019). Particularly interesting is the ability of C-dots to mimic oxidase-like activity even at neutral condition, and thus they break the acidic pH limitations that are characteristic for most artificial nanozymes (Yuxin et al., 2022). The intrinsic nanozyme activity of C-dots opens an opportunity for their utilisation as versatile and environmentally friendly catalysts in numerous applications in ecology and green biotechnology, as well as the possibility to be applied for metal leaching from scrap in the recycling technology. The copper waste from electric and electronic equipment is certainly one of the common metals that might be recycled repeatedly and reused again (Işıldar et al., 2019). In that respect, many eco-friendly and sustainable technologies have been investigated for Cu metal recovery without the use or release of volatile, toxic, or chemically dangerous substances (Needhidasan et al., 2014). In some of them the use of corrosive and oxidant acidic leaching solution remains still a challenge, which is hard to overcome (Babu et al., 2007).

Here we demonstrate the dissolving of metal copper in leaching solution with pH-values around neutral point by employing C-dots as photo-activated oxidase nanozyme. The proposed strategy might break the pH acidic limitations for recycling of copper in the conventional wet chemistry methods. In our experiments C-dots were obtained from citric acid and ethylene diamine via the microwave-assisted pyrolysis, which is a well-studied “Bottom-up” approach (Zhai et al., 2012). Next, ligand-stabilised EDTA-Mn (III) was introduced into the reaction mixture as a mediator that significantly enhances the efficiency of electron transfer in the process (Webb et al., 2005), and thus enhances the rate of copper oxidation and leaching. In the proposed strategy, the formed redox potential of the pair Mn (II) / Mn (III) is 1.54 V, which was strong enough to induce spontaneous reaction of oxidation between manganese (III) ions and Cu⁺ from the metal scrap.

Experimental Procedures

Chemicals and instrumentation

The chemicals used in the experimental section were as follows: ethylenediamine or EDA, anhydrous, NH₂·CH₂·CH₂·NH₂, citric acid, CuH₂O₄ (purchased from Kanto Chemical Co. Inc.), manganese (II) sulphate pentahydrate, MnSO₄·5H₂O.
(purchased from Wako), 4H (EDTA, free acid) or ethylenediamine-N,N,N',N'-tetraacetic acid, C\textsubscript{10}H\textsubscript{16}N\textsubscript{2}O\textsubscript{8}
(purchased from Dojindo, Japan). The water was purified by an Autopure WD 500 (Yamato Science, Tokyo, Japan) through Millipath® 40, Millipore 0.22 µm. A thin metal copper plate with a size of 2 x 11 cm (5.4711 g in weight) was used as a model scrap material. For preparation of reaction solutions were used an analytical balance ITX120, pH-meter AS800 (AXEL, As One, Japan) and magnetic stirrer MS7-H550-S (DLAB, Scientific, Inc., USA). The samples were irradiated with natural sun light and UV-light with irradiation wavelength of 365 nm (Handy UV-Lamp, 100 V, 50/60 Hz, As One, Japan). The absorbance spectra were measured in a quartz cell by an analytical UV-VIS Jasco spectrophotometer (model № V-570).

The change of the colour intensity of the copper leaching concentrate solution was measured periodically at 600 nm by AP-120 photoelectric colorimeter (APEL Co., Ltd., Japan).

Nanoparticle size distribution was determined using dynamic light scattering (DLS, Zetasizer Nano ZS).

Synthesis of oxidase nanozyme

The carbon nanoparticles used in the reported study were prepared via 600 W microwave-assisted pyrolysis of 1 g citric acid and 200 µL ethylenediamine, dissolved into 10 mL of deionised water (Toshev and Loukanov, 2020).

Preparation of copper leaching concentrate solution

The obtained nanomaterials were re-suspended into 150 mL aqueous solution of 0.01 M MnSO\textsubscript{4}. The obtained pH was 2.46. After that 0.5 g EDTA was added into the suspension under energetic mixing by magnetic stirrer, but it remains undissolved at room temperature. The reaction solution was slowly neutralised to pH = 5.1 by dropwise adding of 1.0 M NaOH. At that pH value, all amount of EDTA was well dissolved and the solution turned to transparent. Then, the metal copper plate was inserted on the bottom of the reaction vessel (under the solution surface) and illuminated by either (i) UV-lamp or (ii) the natural sun light (with average intensity of 59 300 Lux). In the second case, the reaction vessel was kept for five days on the laboratory bench close to the window and the change of solution colour was monitored by the absorbance spectrophotometer or photoelectric colorimeter.

During that period there was a gradual change in the colour of the leaching concentrate solution as follows - from light yellow to deep green-blue (after 1 week) and finally to dark-green (after 6 weeks). The solution pH also increased from 5.1 to 7.3 (after 1 week) and to 8.3 (after 6 weeks). At the end of each leaching reaction, the change in weight of the copper metal plate was measured.

Results and Discussion

Nanozyme characterisation

The synthesised nanoparticles are characterised with good solubility in aqueous solution due to the abundance of hydrophilic groups on their surface as carboxyl, amino, hydroxyl, etc. When dispersed into water the obtained solution colour is light yellow as shown on Figure 1A (left side). The nanozyme exhibits absorbance, mainly in the near UV-region with tail of decreasing intensity in the visual range until 600 nm (Figure 1B).

![Fig. 1. Spectrophotometric analysis of the photo-oxidation catalytic leaching of copper from the metal scrap. (A) Photograph taken of the initial leaching solution before the oxidation (left, yellow colour) and after oxidation (right, deep green-blue) of the metal plate. Absorbance spectra of (B) initial leaching solution and (C) the concentrated solution which contained leached copper ions](image-url)
Only two peaks in the UV region were registered, which are located at 256-270 nm and 350-360 nm. They are assigned to the C=C π-π* and C=O n-π* transitions, respectively. Under irradiation with UV-lamp, (365 nm irradiation wavelength) the leaching solution shows bright-blue photoluminescence (PL). PL emission peak is located at 470 nm, and it can gradually shift to longer wavelength with the increase of the excitation wavelength, i.e., the carbon nanoparticles exhibit excitation-dependent PL behaviour in the visual range. Since the absorbance intensity is decreasing toward longer wavelengths, the emission intensity is naturally diminishing too. This suggests that the photosensitising reaction with highest yield of singlet oxygen production must be achieved under irradiation with ultraviolet irradiation. In the case of visible light the yield significantly decreased, and without light irradiation (dark mode) the nanozyme cannot act as photosensitisiser (Zhang et al., 2019), and therefore the copper cannot be oxidised.

Leaching of copper metal

Under optimised conditions (pH 5.1 – 8.3, ambient temperature and sun irradiation with average intensity of 60 000 Lux) the nanozyme exhibits catalytic activity to leach copper metal through singlet oxygen production and use of Mn(III) ions as a mediator. The UV-VIS spectrum of the leaching solution at neutral pH before the reaction of oxidation is shown in Figure 1B. As it is shown with an arrow, no absorbance peak is registered in the visible or near infrared (NIR) range of the spectrum. Such absorbance peak appears around 710 - 730 nm (as shown on Figure 1C) after performing the photo-oxidation reaction with nanozyme and leaching copper in the solution. Thus, further deep green-blue colour was observed, which is assigned to the oxidised Cu(II) metal ions.

The formation of visual deep green-blue colour, as shown on Figure 1A (right side) with absorbance maximum in the VIS and NIR range illustrated the process of slow dissolving of copper metal as Cu^{2+} ions (within 6 weeks as shown with the yellow arrow on Figure 1C). Most of them are existing as Cu-EDTA complex at neutral pH.

A better comparison of the absorbance spectra of the initial leaching solution (solid yellow line as control experiment) and the copper oxidation concentrate (dotted blue line) is presented on Figure 2.

As shown, the absorbance peaks of both spectra in UV range are a little shifted (Figure 2A). If the nanozyme is mixed with MnSO₄ and EDTA, no peak is observed in the NIR region between 600 – 900 nm (Figure 2B, solid yellow line).

Without nanozyme, again no colour change (no peak) was observed during the treatment of copper with EDTA and Mn(II) under light illumination. Nevertheless, when the leaching solution in the presence of the nanozyme was subjected to irradiation with natural sun light within five days, the copper metal plate was dissolved and a peak with maximum absorption approximately 730-740 nm appeared (Figure 2B, dotted blue line). The experimental data revealed that the photo-oxidation reaction effects the absorbance of nanozyme because its peak is shifted from 352 nm to 348 nm (after 1 week) and it is not observable after 6 weeks.

From the spectrum intensity of Figure 2B the amount of leached Cu(II) ions in solution could also be determined via stoichiometry, but the calculated concentration is not equal to the total amount of leached copper, because some of the Cu exists as black deposited oxides on the metal surface. The most accurate way to measure the amount of leached copper was by weight measurement of the metal plate before and after the reaction. All data confirmed that the plate dissolved, but the oxidation speed was slow. For about five weeks we found a reduction in weight from 5.5 g to 5.4 g (~ 0.2 % yield), and after 6 weeks to 5.2 g (~ 5.0 % yield). From a practical point of view, this leaching speed is not yet appropriate for application of the nanozyme in the recycling technology, but the method is still in its infancy.

Reaction mechanism

Because the main focus of reported study was the light-activated catalysis, we turned our attention to understanding the reaction mechanism as shown in the scheme on Figure 3.

\[
\text{nanozyme} + \text{Cu}^{2+} \rightarrow \text{Cu}^{4+} + \text{nanozyme} \tag{1}
\]

Under light irradiation the singlet oxygen \((^1\Delta_g \text{ or } ^1\Sigma_g^+)\) is produced from the nanozyme reacting with ground state oxygen \((^3\Sigma_g^- \text{ or } ^3\Sigma_u^+)\).

\[
\text{nanozyme} \ ^3T_1 + \ ^3O_2 \rightarrow \text{nanozyme} \ ^1S_0 + \ ^1O_2
\]
The short phosphorescence lifetime of \(^1\)O\(_2\) is the reason for its short migration distance and fast deactivation to the ground triplet state.

This problem was solved in our experiments by adding of a ligand-stabilised mediator that can diffuse for a longer time.

The dissolved Mn(II) being oxidised to Mn(III) by \(^1\)O\(_2\), so the formed ions are stabilised by EDTA and further fulfil their role as a mediator for copper leaching. Mn(II) is oxidised to Mn(III) by the dissolved singlet oxygen and the reaction rate was enhanced by adding of EDTA (Zhang et al., 2019).

\[
\text{Cu}^{2+} + \text{O}^2^- + \text{H}_2\text{O} \rightarrow \text{CuO}_2\text{(s)} + 2\text{OH}^- \\
\text{or} \quad 2\text{Cu}(s) + \text{O}_2 \rightarrow 2\text{CuO}_2\text{(s)}
\]

During the process of copper oxidation and leaching the solution pH is rising from 5.1 to 8.3. This indicated that hydroxyl anions were released and/or reaction of neutralisation between the copper oxide and EDTA occurred:

\[
\text{CuO}_2\text{(s)} + \text{EDTA} \rightarrow \text{Cu}^{2+}\text{EDTA} + \text{H}_2\text{O}
\]

**Thermodynamic calculations**

The calculations related to the overall thermodynamically favourable reaction between manganese and copper in the leaching solution, i.e. copper oxidation by Mn(III), are presented below:

\[
\text{Cu}(s) + 2\text{Mn}^{3+}\text{(aq)} \rightarrow \text{Cu}^{2+}\text{(aq)} + 2\text{Mn}^{2+}\text{(aq)}
\]

For this reaction the number of moles of electrons transferred per mole is \(z = 2\).

**Oxidation process:**

\[
\text{Cu}^{2+}/\text{Cu}, E^\circ = + 0.34 \text{ V}
\]

**Reduction process:**

\[
\text{Mn}^{3+}/\text{Mn}^{2+}, E^\circ = + 1.54 \text{ V}
\]

The standard cell potential \(E^\circ\text{cell}\) at 298 K is:

\[
E^\circ\text{cell} = [E^\circ\text{red}] – [E^\circ\text{ox}] = 1.54 \text{ V} – 0.34 \text{ V} = 1.20 \text{ V}
\]

The corresponding Gibbs energy is:

\[
\Delta G^\circ = – zFE^\circ\text{cell} = – 2 \times 96 485 \times 1.20 = – 231 564 \text{ J}
\]

\[
\Delta G^\circ = – 232 \text{ kJ per mole of reaction}
\]

The equilibrium constant \(K\) is:

\[
\text{ln}K = – (\Delta G^\circ/RT) = – (–232 / 8.314 \times 10^{-3} \times 298) = 93.66
\]

Therefore, the reaction between the catalytically produced Mn(III) and Cu(s) is spontaneous at ambient temperature, because the value of \(E^\circ\text{cell}\) is positive, \(\Delta G^\circ\) is negative and \(K > 1\). As confirmed previously, Mn(II) can be oxidised to Mn(III) by the dissolved oxygen which is converted to \(^1\)O\(_2\). The presence of singlet oxygen was confirmed in our previous report by its phosphorescence emission at 1275 nm (Toshev et al., 2020). Based on the thermodynamical calculations we have assumed that the catalytically produced Mn(III) is responsible for the oxidation of copper metal at pH = 5.1 – 7.3 (neutral conditions). In general, Mn(III) ions are unstable in aqueous solution and that was the reason to be stabilised by EDTA ligands. Under illumination with natural sun light the colour of the leaching solution changes from yellow to blue within few days. By using UV-lamp the result might be achieved even for shorter time.

**Conclusion**

In this report the photo-catalytic performance of N-doped C-dots as an oxidase-mimicking nanozyme to leach copper was investigated. To the best of our knowledge there is no any other nanozyme-induced oxidation of copper at neutral pH under natural sun light irradiation. The obtained results demonstrated that the leaching speed was too slow and not appropriate yet for the nanozyme application in the recycling technology. Nevertheless, the method is still in its infancy and deserves further studies.

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**References**


GEOLOGICAL RISK MANAGEMENT PROCESS AND ITS PARTICULARITIES FOR A URANIUM SITE - CASE STUDY

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ABSTRACT. Anthropogenic radioactive pollution of the environment resulting from the research and exploitation of uranium resources is a topical issue for the scientific community because it represents a threat to people's health conditions and has a highly negative impact on the environment. The sources of radioactive pollution are due to the presence of low-level radioactive tailings and poor ore dumps resulting from the exploration and exploitation of uranium ore deposits. Uranium under the action of environmental factors can reach the groundwater, the river network, and the food chain, respectively. The contaminated food and water may cause diseases and even cancer. An important role in the pollution spreading is played by geological phenomena, the most important being landslides. Thus arises the need for geological risk management. The present study aims to implement a geological risk management system through methods of assessment, monitoring, and prediction of geological risk for a chosen uranium site. The waste rock and water samples analysis pointed out the radioactive contamination risk. The simulated scenarios in the area exposed to subsidence phenomena showed the activity of increasing the concentration of radioactive waste in the hydrographic system's groundwater in the studied site, in a time interval of 4120 days (11.29 years); it rapidly increased in the first 1000 days (from 0.0 to 0.0033), after which it decreased in intensity until day 2500 (from 0.0033 to 0.00048), and it is supposed to stagnate after day 4120 when the simulation ended. The results emphasised the radioactive contamination spreading risk in the case when the subsidence phenomenon takes place.

Keywords: geological risk, uranium mining site, landslides, monitoring of geological parameters

Introduction

Anthropogenic radioactive sources that have occurred in the environment due to uranium resources' research and exploitation were inappropriately managed during the time. The interaction between existing sources of radioactive pollution on sites or in underground mining works and natural phenomena generating geological risk can particularly amplify the destructive effects on communities and natural habitats, which can persist in the very long term; remedial measures are currently very expensive and unfeasible.

In this context, the geological risk management process can be an effective method of preventing radioactive pollution of the environment.

The implementation of modern methodologies used internationally in the forecast of landslides that occur on tailing dumps in the uranium mining sites may result in reducing the geological and radiological risk (Mejia-Navarro, 1994; INCDMRR, 2006-2009). Getting the most accurate prediction results makes it possible to reduce the vulnerability degree of receptors in the influence area.

The chosen area as a case study in this paper is the Avram Iancu uranium mining site in the Arieșului Mic basin, Alba County.

In this study, determinations of the gamma dose on the dumps in the chosen site were used to measure the radioactive contamination.

Chemical analysis of samples taken from rocks deposited on the dump, soils, and waters, determinations of Rn concentrations on the dumps' surface and at the entrance of accessible galleries; besides performing laboratory tests to determine radioactive elements were also applied.

Methods and equipment

Landslide forecasting is achieved through different types of approaches: deterministic, direct, indirect, statistical, and GIS (Van Westen, 2004):

- deterministic methods are based on the calculation of the stability factor;
- direct methods aim at positioning landslides on maps and making landslide distribution maps;
- indirect methods are based on the analysis of the conditions of occurrence (slope, lithological, land use) of landslides;
- statistical and GIS methods are used to process and interpret data obtained by direct and indirect methods (Ayalew, 2005).

Gamma radiation is emitted by radionuclides contained in waste rock deposited in dumps or poor ore deposits (Baeza and Corominas, 2001).

Radon 222 is a radioactive gas found on the surface of uranium-poor tailings or ore deposits and has a high degree of risk and is associated with 15% of lung cancer cases. Zajzon and co-authors (2015) pointed out the presence of heavy metals in the studied area.

Infiltration from tailing dumps can contaminate surface water and groundwater with Radium 226, but also with other substances occurring in the uranium deposit (heavy metals, arsenic, pyrite) (Zajzon et al., 2015).

The determination of gamma radiation in the field was performed with the FAGFH40F2 radiometer, with a sensitivity of 0.01 µSv / h.

The determination of uranium, radium, thorium, and cesium in soil and sediment samples was performed in parallel by...
gamma spectrometry, with the four-channel analyser type NP 424 and with the multichannel analyser type ORTEC-2000 with Ge Hyper-pure detector.

Results and discussions

Characterisation of the studied mining site

The Băiţa-Avram Iancu exploitation zone is delimited to the north (Figure 1) by the confluence of the waters between Valea Calului and Crişul Băiţa; to the south by the confluence of the waters between Valea Leucii and Piatra Aradului; to the east by the Bihor Peak and by the springs of Arieş Mic and by the left slope of Arieş; to the west by Tăul Mare Peak and by the springs of Dedeşului brook and Dibarz brook. From a territorial administrative point of view, the exploitation site is located at the border between Bihor, Alba, and Arad counties, but it belongs to Bihor County.

In the Bihor mining site (Băiţa, Avram Iancu) which occupies an area of 50 km$^2$, there is a multitude of mineralisations with different genesis from U and Mo, W, Bi, Ni, Co, Pb, Cu, Ag, Zn, B (Figure 2) (Zajzon et al., 2015.)

![Fig. 1. Mining site location and access roads (adapted from INCDMRR report)](image-url)
Tailing dumps in the Avram Iancu site (Arieşului Mic basin - sector North) (Figure 3), where G stands for gallery, are as follows:

- **Dump of G X North:** made up of waste rocks dominated by quartz-feldspar shales.
- **Dump of G XX:** it consists of the tailings from the underground penetration works on the surface of the XX horizon, now it is naturally restored from an ecological point of view.
- **Dump of G XII gallery:** consists of waste rocks dominated by quartz-feldspar shales and chlorite shales.
- **Dump of G I Arieş:** The entrance of the gallery is located on the right slope of the Arieşului Mic valley, about 1.5 m above its riverbed.
- **Dump of G VI Arieş:** Located on the right side of the Arieşului Mic Valley, it occupies an area of about 950 m² and it is the result of the excavation of gallery VI located at an altitude of +1140 m.
- **Dump of G XI Vechi şi Nou:** The tailings from the opening of the old XI gallery (elevation +1120 m) were deposited in the bed of the Arieşul Mic stream, respectively on either side of the gallery. The base of the gallery is about 1 m higher than the bed of Arieşului Mic.
- **Dump of the G XII Arieş:** The gallery started from the surface at an altitude of +1121 m; it is located on the right slope of the Arieşul Mic Valley.
- **Dump of the G XVI Bis:** The dump has a large size occupying an area of 15,500 m² and it was used to store the tailings resulting from the opening and preparation of the ore bodies.

**Obtained results**

Within the Avram Iancu mining site, the following research was carried out: field measurement of the gamma flow dose on dumps; sampling of rocks deposited on the dump, soils, and waters; determination of Rn concentrations on the surface of dumps and at the entrance of accessible galleries; laboratory analyses for the determination of radioactive elements (U, Ra, Rn).

The data obtained were displayed in Tables 1 and 2 or were subsequently represented in two dimensions as distributions of gamma parameters on the measured area (Figure 4).

The data displayed in Table 1 pointed out that the highest content of U and Ra was recorded in the leakage from G XII, namely, 0.105 mg/L and 0.070 Bq/L, respectively. Therefore, the radioactive contamination risk is high.
Fig. 3. Location of tailings dumps in the area of the Avram Iancu mining site - North

Table 1. Mining with seepage in the receiver (Arieşul Mic)

<table>
<thead>
<tr>
<th>No.</th>
<th>Name of the work</th>
<th>Flow (L/s)</th>
<th>Minimum flow of the receiver at the point of emergence (L/s)</th>
<th>Content in items radioactive</th>
<th>Spill into the environment (stream)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>P = 95%</td>
<td>U (mg/L)</td>
<td>Ra (Bq/L)</td>
</tr>
<tr>
<td>1</td>
<td>G. XII</td>
<td>1.5</td>
<td>15.6</td>
<td>0.105</td>
<td>0.070</td>
</tr>
<tr>
<td>2</td>
<td>G. Arieş</td>
<td>0.04</td>
<td>15.6</td>
<td>0.008</td>
<td>0.009</td>
</tr>
<tr>
<td>3</td>
<td>G. XI Vechi Arieş</td>
<td>3</td>
<td>17</td>
<td>0.075</td>
<td>0.058</td>
</tr>
<tr>
<td></td>
<td>MAC* drinking water according to STAS** 1342/91</td>
<td></td>
<td></td>
<td>0.021</td>
<td>0.088</td>
</tr>
</tbody>
</table>

*MAC= maximum admitted concentration and **STAS = Romanian standard that regulates U and Ra content in drink water in Romania

The data from Table 2 showed that dump G VI has the highest content of uranium and radium (850 g/t and 11.86 Bq/t, respectively) confirming the radioactive contamination as well.

The 3D model database includes geological maps and sections, data from geotechnical drilling, vector information, numerical models, hydrogeological data, and temporal information as shown in Figure 5.

All the information is extremely useful to model the northern sector of the Avram Iancu mining site.

The next steps required to build the three-dimensional model for the Avram Iancu mining site - the northern sector were (Figures 6 and 7): obtaining the digital terrain model; overlapping external elements on the digital surface model: tailings dumps, hydrographic network (Arieşul Mic stream),
Table 2. Radiometric measurements and radionuclides determination on dumps

<table>
<thead>
<tr>
<th>Name / location/ elevation</th>
<th>Surface (m²)</th>
<th>Maximum content in radioactive elements</th>
<th>Maximum gamma dose rate (μSv/h)</th>
<th>The value of the maximum concentration of Rn (Bq/m³)</th>
<th>Stored material</th>
<th>Location relative to watercourses</th>
<th>Surface with gamma dose rate values &gt; 0.3μSv/h* (m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dump G. X North 1181 m</td>
<td>850</td>
<td>10</td>
<td>0.05</td>
<td>0.03</td>
<td>35</td>
<td>Crystalline shales from the Biharia series</td>
<td>On the right slope of the Arieșului Mic valley</td>
</tr>
<tr>
<td>Dump GXII East 1153 m</td>
<td>1800</td>
<td>4</td>
<td>0.03</td>
<td>0.45</td>
<td>40</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Dump G.I 1164 m</td>
<td>1200</td>
<td>70</td>
<td>0.7</td>
<td>0.65</td>
<td>75</td>
<td></td>
<td>70</td>
</tr>
<tr>
<td>Dump GVI 1140 m</td>
<td>950</td>
<td>850</td>
<td>11.86</td>
<td>1.9</td>
<td>370</td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>Dump G. Arieș 1134 m</td>
<td>160</td>
<td>15</td>
<td>0.047</td>
<td>0.25</td>
<td>25</td>
<td></td>
<td>Near the Arieșului Mic valley</td>
</tr>
<tr>
<td>Dump G.XI Nou 1120 m</td>
<td>1955</td>
<td>12</td>
<td>0.1</td>
<td>0.55</td>
<td>50</td>
<td>On the right slope of the Arieșului Mic valley</td>
<td>75</td>
</tr>
<tr>
<td>Dump GXIII 1121 m</td>
<td>7500</td>
<td>36</td>
<td>0.23</td>
<td>0.28</td>
<td>38</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Dump GXVI bis 1130 m</td>
<td>15550</td>
<td>150</td>
<td>1.25</td>
<td>1.02</td>
<td>145</td>
<td></td>
<td>2100</td>
</tr>
</tbody>
</table>

*Maximum admitted limit for gamma radiation dose rate in ecological reconstruction

Fig. 4. Distribution of the gamma dose on the main dumps of the Avram Iancu mining site

Fig. 5. Integration of geospatial information into the 3D model database

closure works at the surface (gabion walls, closing plates for open wells); realisation of the network of underground mining works (directional, transversal galleries, open wells and blind wells, sloping planes); reconstitution of mineralised bodies that have been exploited; realisation of the 3D model of the geological structure including the known tectonic elements (Chung and Fabbri, 2002). Specialised software was used in the steps listed above: Global Mapper, AutoCad, QuickSurf, GoCAD, Interdex, GoogleSketchup, and ArcGis.
Spatial representations required for the design of the monitoring network

The technique of SAR interferometry (InSAR) is known for the speed and accuracy of collecting topographic data. Synthetic Aperture Radar (SAR) images contain both the amplitude and the phase of return signals from the Earth’s surface.

Through a special algorithm and manual editing, the landscape elements are removed, and the digital terrain model is generated.

Due to the non-existence of topographic plans in electronic format, the situation plans of the site at a scale of 1: 2000 were used. This plan was scanned to an appropriate resolution so as not to lose important details, and the resulting file was uploaded to Global Mapper software version 9 and georeferenced after the grid on the Stereo 70 projection system.

The 10 m curves were digitised and assigned the corresponding elevation value of the elevation and then used to check and correct the elevations. Also, a capture of spatial coordinates was made on a network with a resolution of 10 m in the site area (Figure 8) by using a specialised extension under ArcGis that allows obtaining in KML format a series of coordinates in geographical format from the Google Earth.

Once the database is obtained by inventory, thus knowing the situation at a given time, we move on to the study of susceptibility, i.e., to the definition of areas that may be prone to landslides (areas with subunit safety factors).
Due to the increased permeability of the material in the area of the sinking bed (Figure 15) and due to the stretching and compression, this can be a path of draining rainwater or torrential water loaded with radioactive contaminants due to washing waste dumps or poor ore deposits that have not been completely evacuated. Thus, the integrated GIS system can point out, for different profiles chosen automatically or by the user, the exceeding of some alert thresholds regarding the evolution of certain parameters of the subsidence.

The processing performed with the help of the subsidence module, the two- and three-dimensional graphical representations (Figures 16 and 17), and the dynamic evolutions through the integrated GIS system can be used to predict this geohazard phenomenon and the drawing of thematic risk maps to be used in estimating vulnerability to environmental factors and habitats. The obtained results can show the areas exposed to risk, areas that can amplify the radioactive contamination of the environment by leaching into the local hydrographic system or in the underground waters of some waste with radioactive loading (Figures 18 and 19).

In the contamination source’s area, the drilling was located to monitor the source’s concentration and downstream were located another 5 boreholes for monitoring the concentrations of U and the piezometric level.

Figure 18 shows the area exposed to subsidence phenomena and Figure 19 the activity of increasing the concentration of radioactive waste in the hydrographic system’s groundwater in the studied site, in a time interval of 4120 days (11.29 years):
Fig. 15. 3D representation of the sinking bed (mining subsidence) for the monitored location

Fig. 16. Discretisation of the deposit in calculation blocks for calculating the subsidence

Fig. 17. Horizontal deformation dependence on the time variation for a landmark in the mining subsidence monitoring network
Fig. 18. Areas exposed to subsidence phenomena in the site Avram Iancu - Ariesul Mic basin

Fig. 19. Simulation of U radionuclide dispersion in groundwater (source of continuous contamination, steady flow)
It has an accelerated increase in the first 1000 days (from 0.0 to 0.0033), after which it decreases in intensity until day 2500 (from 0.0033 to 0.0048), and it will stagnate after day 2500 until day 4120 when the simulation ended.

With some control data of the contents of the boreholes or even of the wells, it is possible to calibrate the concentration of the contaminant to have some information that is somewhat relevant for the proposal of a monitoring network.

**Drawing hazard maps when slipping**

Two methods were considered, namely statistical analysis and deterministic method with modelling of local geological, hydrogeological, and seismic conditions (Paudits, 2002, Remongo, 2005, Thywissen, 2006).

The statistical method for the execution of slip hazard maps is based on quantitatively determined weighted values. With the help of these maps, different scenarios related to the stochastic evolution of the parameters with an impact on the triggering of geohazard phenomena: hydrogeological, geological, and seismic parameters (Figure 20).

The steps followed in the evaluation of the slip hazard were: intercorrelation of the slip maps with the parameter maps; for each category (e.g. lithological units, slope class) the weighted value is calculated (the ratio between the natural log of the slip density on the respective class and the slip density for the whole map - Figure 21): slips will be less than a normal threshold value, and weighted values will be positive when the slip density is higher than the threshold value, by algebraically summing (or by other defined criteria) the weighted maps.

![Slope map](image1)
![Sensitive clay thickness map](image2)
![Dry state](image3)
![Saturated state](image4)

**Fig. 20. Scenarios related to the stochastic evolution of the parameters with impact on the onset of geohazard phenomena**
Conclusions

The implementation of modern methodologies in the forecast of landslides that occur in the dumps in the uranium mining sites can result in a decrease in geological and radiological risk. Making predictions as accurate as possible can decrease the degree of vulnerability of the receptors in the influence area.

The need to represent and analyse large informational volumes of spatial (georeferenced) and non-spatial data on the short and long-term assessment of the risk induced on the environment and implicitly on human communities by former uranium mining, requires the use of software applications GIS. Hazard (landslide, subsidence, flood, earthquake, contamination) mapping techniques are implemented through separate modules or procedures within the GIS geological risk management platform and are based on stochastic or deterministic methods.

With the help of these maps, different scenarios related to the stochastic evolution of the parameters with an impact on the onset of geohazard phenomena can be made later, to reduce or even eliminate the negative effects induced on the environment or the human community by uranium sites.

The simulated scenarios in the area exposed to subsidence phenomena showed the activity of increasing the concentration of radioactive waste in the hydrographic system’s groundwater in the studied site, in a time interval of 4120 days (11.29 years): it rapidly increased in the first 1000 days (from 0.0 to 0.0033), after which it decreased in intensity until day 2500 (from 0.0033 to 0.0048), and it is supposed to stagnate after day 2500 until day 4120 when the simulation ended. The results pointed at the radioactive contamination spreading risk in the case when the subsidence incident takes place.

Acknowledgments
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References
CONVERTING COAL MINING INTO UNDERGROUND PRODUCTION OF ARTIFICIAL OIL

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ABSTRACT. A method for direct liquefaction of coal is presented. After separating the coal from waste rock gravitationally in an aqueous salt solution, drying and grinding, the purified separated coal is mixed with a paste-forming reagent. The paste is ground until a colloidal particle size and hydrogenated for 2 hours at temperature of 405°C and 11 MPa hydrogen pressure. Artificial oil was obtained with over 95 % yield with respect to the initial amount of purified coal when the contact of excavated coal with air was avoided. Based on findings, a technology is proposed for underground coal liquefaction with significantly reduced energy consumption of the process, removed environmental hazards and higher efficiency with respect to existing technologies.

(Key words: coal liquefaction, synthetic oil, underground)

Introduction

Humankind needs oil - for industry development, transport and trade, and for its normal everyday life.

In refineries different parts of the crude oil are separated into useable petroleum products, such as gasoline, distillates (diesel fuel and heating oil), jet fuel, petrochemical feedstocks, waxes, lubricating oils, and asphalt - https://www.eia.gov/energyexplained/oil-and-petroleum-products/.

So, oil is needed to generate electricity to light our homes, run factories and machines, as a raw material to produce fertilisers to increase food production, etc.

For example, in 2020 the USA petroleum accounted for 34.7% of energy consumption and was used mainly in the transportation, manufacturing, and electricity sectors (USEIA, 2022).

Another example, in 2021, the total gasoline consumption (based on energy content) accounted for about 58% of transportation sector total energy consumption and 16% of U.S. total energy consumption, and (based on volume) 45% of total petroleum consumption - https://www.eia.gov/energyexplained/gasoline/use-of-gasoline.php.

However, the oil price is steadily increasing - Figure 1.

![Fig. 1. Oil price development in 35 years. Source: https://tradingeconomics.com/commodity/crude-oil, accessed 29.06.2022](image)

The problem with oil prices and shortage is not a recent one. It was posed more than a century ago. The scientists and engineers searched for engineering means for using scientific knowledge for applied purposes, namely to produce synthetic oil (Burke et al, 2001; Mitchell, 2008; Vasireddy et al., 2011; Towler, 2014).

As early as 1913, more than 100 years ago, a great German chemist Friedrich Bergius was the first in the world to obtain artificial liquid fuel from coal in laboratory conditions (Schulz, 1999). The idea of the method consisted in catalytic hydrogenation of coal under the action of hydrogen at high temperature and high pressure in the presence of a solvent. The solvent facilitates coal extraction and the addition of hydrogen. The solubilised products, comprising mainly of aromatic compounds, are further upgraded by conventional petroleum refining techniques such as hydrotreating to meet final liquid product specifications (Burke et al, 2001). In 1931, Bergius was awarded the Nobel Prize in chemistry for his "merits in the introduction and development of a high-pressure method in chemistry".

During World War II, 18 plants were built in Germany and worked for coal hydrogenation (with 95 000 employees), liquefying annually 50 million tons of lignite and 10 million tons of coal. 92% of aviation petrol consumed by Luftwaffe were of synthetic origin (Schulz, 1999).

Indeed, such artificial fuel was about 10 times more expensive than natural liquid fuel obtained from natural oil.

In the modern epoch, the attention to the problem of coal liquefaction was attracted again in 1973, when Egypt and Syria declared during the October war at the Middle East that they would not supply oil at former prices to the countries that supported Israel in this conflict. This made Western governments activate researches in the field of coal processing into artificial liquid fuel.

On the other hand, nuclear tragedy of Chernobyl and Fukushima disaster led to an obvious apathy with respect to atomic power engineering all over the world.

Note that only 2% of integral coal resources have been exhausted (for comparison, 85% of total oil resources in the world have been already exhausted) (Sharovar, 1989).

Therefore, it is no wonder that efforts aimed at the search for more perfect methods of coal liquefaction are activated again.

The greatest recent achievement in this direction is the largest, on a global scale, plant producing artificial liquid fuel
constructed in China (Shenhua Ordos DCL Project, Inner Mongolia) (Plaza and Pevida, 2019).

The analysis of prime cost of finished product of this plant shows that about a half of all expenses in the total structure of its production costs falls on coal purchase and transportation to the liquefaction spot.

All this suggests a conclusion that new ways of cardinal reduction of underground mining price are needed, coupled with a complete denial of drawing coal (produced at a much lower price) to the ground surface and usage of highly efficient and compact methods of its underground direct processing into synthetic oil in the immediate vicinity of the mining face.

In contrast to silica sand or other oxygen-containing rock formations, coal is not a chemically inert material and its contact with oxygen irreversibly leads to gradual processes of endogenous oxidation, resulting in loss of not only calorific value, but also in decrease of synthetic oil yield during liquefaction of the solid fuel.

Therefore, the main object of the study was not only finding new, non-energy-intensive ways of underground coal mining, but also development of compact and precise methods for ultra-clean coal concentrates production directly in underground conditions, and identifying the correlation between the contact of freshly mined coal with oxygen in air and the effectiveness of its liquefaction.

Here, we propose such a method of coal mining and precise beneficiating with its subsequent underground liquefaction.

Materials and methods

Coal processing was carried out in the laboratory by the following methodology. Freshly mined from the working face regular raw coal (ash content 8.9%, volatile matter content of 45.2%, and sulphur content of 0.8%) was immediately immersed in a jar with an aqueous solution of Lewis acids, 45.2%, and sulphur content of 0.8%) was immediately taken into a jar with an aqueous solution of Lewis acids, thereby avoiding additional irrational energy costs for their aggregates with gangue and floated to the surface of the liquid, thus avoiding additional irrational energy costs for their aggregates with gangue and floated to the surface of the liquid, through the layer of such aqueous solution, a continuous phase, only practically clean from mineral impurities pure coal will float to the surface of the heavy liquid medium in the thermally insulated mill.

The hot suspension of the ground coal discharged from the thermally insulated ball mill, was separated in a high-speed (4000 rpm) laboratory centrifuge. The cake, pressed by centrifugal forces into the surface of the inner rotating rotor, was discharged from the centrifuge by a rotating screw, cooled, and returned to the steel mortar for mixing with the next batch of the raw mined mass. The centrifuge concentrate, which is a suspension of deeply purified from mineral impurities coal, was separated using a filtration centrifuge.

Without waiting for the wet cake pressed on the filtration centrifuge to cool down, 108 grams of the material was collected, which corresponded to a net of 100 grams of dry, demineralised solid carbonic material, and mixed with 200 ml of hot (160 °C) paste-forming agent, which is a mixture of (90:10 by volume) tetralin (1,2,3,4-tetrahydro-1-naphthalene—C14H12) with anthracene oil (a fraction of coal-tar resin boiling within the range 270-360 °C). In addition, during the mixing process almost complete removal of water vapour from the prepared paste occurred and was evacuated with a vacuum pump.

Then, to the paste obtained in the above manner and cooled to 80 °C, 100 ml of isopropyl alcohol was added, and a dilution of the mixture was carried out in a high-speed mixer. The diluted with isopropyl alcohol paste was then sent to a centrifugal disperser in which additional grinding of the solid phase of the system was carried out until a colloidal particle size was achieved. After this, the content of the disperser was reloaded into a steel autoclave, placed in a muffle furnace with a tangential inlet of compressed hydrogen (for a more efficient mixing), carrying out hydrogenisation of coal in the medium. For this purpose, the mixture in the autoclave was gradually heated from 80°C and initial hydrogen pressure of 2 MPa to the temperature of 405°C and 11 MPa hydrogen pressure.

After 2 hours of hydrogenisation, the autoclave was removed from the muffle furnace, cooled, unsealed, and the formed synthetic oil was separated from solid particles using the filter centrifuge. The extracted solid precipitate from such liquid was washed from the residues of synthetic oil with petroleum ether and dried with hot air, then sufficiently washed with warm distilled water, dried, and weighed. This material was directed to mixing with the cake received from pressing of the heavy product of the first stage of grinding on the Nutsche filter. The obtained tailing mixture of solid minerals was washed with hot fresh water using the Nutsche filter and removed from the process as waste. The formed washing water was mixed with the discharge of washing of the solid residue separated from the synthetic oil and evaporated to adjust the density of the salt-water solution to its initial value of 1,417 g/cm³.

Figure 2 presents a scheme of the procedures carried out.

Similar experiments were carried out exactly with the same procedure and for the same coal, but already delivered to its destination by a railway from the place of mining.

...
The produced oil was characterised using the spectrometry method. All analyses for the content of the main five elements were performed using an optical emission spectrometer with a rotating disk electrode SpectrOil 100 (RDE-OES).

Fig. 2. Scheme of the experimental procedures carried out

Results and discussion

The dry residue from the autoclave weighed 2.74 grams. Since the autoclave was loaded with paste prepared according to the procedure described above, containing 100 grams of pure feedstock, the degree of liquefaction of the material which entered to hydrogenisation was 97.26%.

The degree of liquefaction obtained in the experiments carried out for the same coal, but already delivered to its destination by a railway, was equal to 82.48 - 83.56%, that is 13 - 15% lower than of coal freshly extracted in the mining face.

The elemental composition of the obtained synthetic oil is characterised by the following data (%): C - 79.2, H - 8.3 and (O+N+S) - 12.5. The most valuable part of the obtained artificial oil is the fraction of neutral oils. It makes up at least half of the product obtained and is significantly enriched in hydrogen compared to the original artificial oil and it has less ballast (O+N+S). Its composition, in % is C - 83.5, H - 9.0 and (O+N+S) - 7.5.

Based on the analyses the non-refined produced oil can be classified as paraffin-naphthenic type oil. The following microelements were found in the composition of artificial oil: Cr; Sb; Ni; Sc; Zn; Co; Fe; Hf; Re.

At the same time, the content of these micro-impurities is so insignificant that they are not able to have a harmful effect on the processing of such raw materials.

The methane release can be gathered thus contributing to the multipurpose use of the coal, and liquefaction becomes more complete (due to the supply for hydrogenation of super-high purity coal concentrate thoroughly impregnated, besides, by a hydrogenation catalyst). This essentially decreases the specific consumption of the initial raw material per each ton of the obtained liquid product.

Based on the results from above-described and other experiments a technology has been proposed for underground liquefaction of combustible material (Brodt, 2016) - schematically presented in Figure 3.

Fig. 3. High level schematic illustration of subsystems in the combustible material processing system

It is proposed the liquefaction process to be carried out underground using directly excavated coal and other combustible materials.

At that, harmful effect of underground mining and artificial liquid fuel production of the natural environment considerably weakens, since all final tailings of coal beneficiation and solid waste of artificial liquid fuel production remain in the underground worked-out space.

Besides, the denial of drawing crude solid fuel from coal mines to the ground surface and shipping the ready product in the form of artificial oil obtained in underground conditions, make it possible not only to abolish from the mine economy
such powerful electric power consumers as rope-skip hoists (the power of modern mine hoists reaches up to 15,000 kW) and coal-beneficiation factories (total electric power of the drives of all kinds of basic technological equipment installed at such ground-based production units can reach up to 10,000 kW), but also to wholly reject the services of railway transport. The mechanical losses of solid fuel due to the coal dust blowing by wind from the wagons is also avoided.

In this case, it is much more profitable to deliver the production to its destination by pipeline transport, which is about three times cheaper than coal transport by railway (not to mention mechanical losses of solid fuel due to coal dust blowing out of railway cars by wind).

Such proposal is of special interest for developing deep and extra-deep deposits of energy minerals. For instance, today the record depths reached by modern coal-mining industry are close to 2000 meters. Coal liquefaction at such extreme depths automatically leads to the working pressure growth in the zone of its hydrogenation up to $21 + 22$ MPa (without bringing in any power inputs from outside). This significantly intensifies such underground technological process and drastically facilitates the conversion of even the most coalified kinds of combustible minerals into artificial oil.

However, according to today's geological data, coal series cover much greater depths. This fact opens prospects of developing these huge supplies of energy minerals for converting mining from coal (solid fuel) production to ecologically clean production of synthetic liquid fuel instead.

With deepening level of underground mining, a steady growth of the bearing strata temperature allows a considerable increase in the share of free heat of the interior of the Earth in the total energy balance of such technological process.

We cannot ignore the fact that the saturation of coal and bearing strata with methane with growing coal seam depth also drastically increases. In this connection, the possibility of complex usage of the energy potential of the produced raw mineral by simultaneous methane extraction assured by the proposed method, also advantageously distinguishes said method from known technologies of solid fuel processing into alternative energy carriers.

A significant contribution to the profitability of underground coal liquefaction in comparison with ground-based production of artificial liquid fuel is due to a reduced hydrogen demand, since energy minerals freshly produced from the mining face are immediately isolated from the mine atmosphere by liquid medium. Thus, since the very beginning of coal separation from the mining face, air oxygen automatically loses contact with the coal component of the combustible mineral and does not trigger the mechanism of its irreversible endogenic oxidation.

Meanwhile, the conventional approach to the production of artificial liquid fuel with coal liquefaction system located on the ground surface, far from the coal supplier, and deepening of underground mining, on the contrary, leads to an irreversible growth of the prime cost of the obtained artificial liquid fuel and to the growth of harmful effect of such human industrial activity on the natural environment.

Conclusion

The use of the proposed method in the coal industry as energy-saving and environmentally friendly, using underground, and not above ground production of synthetic liquid fuel from such carbonaceous raw materials, promotes significant improvement of technical and economic efficiency of processing of such fossil fuels, particularly characterised by high content of non-combustible mineral impurities in it.

At the same time the method provides a comprehensive utilisation of the produced coal (due to deep extraction from the raw material and extraction of methane) and increase in the degree of its liquefaction (due both to the elimination of contact with oxygen in the air and addition of ultra-high purity coal concentrate, thoroughly soaked with catalyst of the hydrogenisation process, to the hydrogenisation). This significantly reduces primarily the specific consumption of raw solid fuel for each ton of liquid product.

In addition, the harmful effects of the whole complex of underground mining and production of synthetic liquid fuels on the environment are greatly reduced, as all final tailings of coal beneficiation, as well as solid waste from the production of synthetic liquid fuels, will automatically remain in underground mined-out space.

Moreover, the rejection of lifting raw solid fuel to the earth's surface from the coal mines, but lifting of finished products in the form of synthetic oil (or even the primary products of its processing) obtained in the underground conditions, allows not only to annihilate such powerful consumers of electricity as the cable-skip hoist and coal preparation plants from mine, but also completely abandons railway transport services. In this case, for coal producers it is much more profitable to use a coal pipeline for delivery of their product to the place of its destination, which is about three times cheaper than coal transportation by railway.

The complete economic triumph of the underground liquefaction of coal is determined not only by the progress of chemical science, but also by the progress of mining. In particular, the processes of unmanned development of coal deposits have already been invented, which can reduce the cost of coal by 2-3 times. Only in the combination of these two conditions is the final goal achieved - a fundamental change in the very purpose of the coal industry from the issuance of coal to the earth's surface to the pumping of artificial oil from the mine.

The depth of the coal also plays an important role. As the depth increases, the hydrostatic pressure of the column of oil suspension supplied for hydrogenation increases. Thus, the deeper the mine, the easier the process of coal liquefaction.

On the whole, the main advantage of the proposed technological process is a steady growth of technical and economic efficiency of underground coal liquefaction with growing depth of coal production.

References


COMPARISON OF SIMULATION MODEL AND PLANT DATA OF A CRUSHING - GRINDING CIRCUIT

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ABSTRACT. Increasing complexity of ore deposits requires operations to be continuously improving their cost competitiveness. Mathematical modelling and process simulation techniques are useful tools to understand the process, define bottlenecks and increase process efficiencies. This paper presents a crushing and grinding circuit of a chromite ore gravity separation plant’ simulation model results and actual plant operating data. Throughout the study, jaw crusher, ball and rod mill summary equipment characteristics, breakage and selection functions employed, comparison of particle size distribution curves of site process streams to model results are presented. Simulation work is completed by using METSIM® software. The paper also showcases ease of flow diagram and process data presentation by the utilisation of the adequate simulation approach.

Key words: crushing-grinding circuit, chromite ore, process simulation, breakage, selection function

Introduction

Modelling and simulation application to process plants has an important role in operational and business case development. Relying solely on engineering estimates or vendor information lacks interdependent technical data of the plant streams, and dynamic interaction of each stream with one another.

Process simulation also allows experimenting various process options within fewer time frames and with more precise results compared to the spreadsheet approach. It provides having the process flowsheet, mass or energy balances, particle size distributions, plant discharge mediums in any phases, or energy consumptions under one roof. Employing simulation software enables the users to change any process parameter quickly without having to edit upstream or downstream formula connections. Additionally, using adequate software and simulation approach provides getting outputs from one resource that would easily provide input for other project departments such as finance by providing OPEX or CAPEX data, or discharge tonnage with contaminants for environmental department.

Presented simulation of the crushing and grinding circuit demonstrated the ability to consider many variables simultaneously. Throughout the paper, process streams sampling results for particle size distribution were compared to the simulation results and main equipment characteristics used as input for the simulation model were shown.

Materials and methods

Processed ore that is subject to this study is a chromite ore with average feed grade of 12%. Ore body is associated with serpentine and olivine minerals. Chromite particles are in round shapes with sizes between 50 µm and 1600 µm with average size of 450 µm.

SEM picture of the chromite particles is shown on Figure 1. Plant crushing (partial) and grinding circuit are presented on Figure 2 and Figure 3.

Jaw crushers are generally employed as first stage crushing for the size reduction of large size ore.
This type of crusher primarily operates as compression crusher (Gupta and Yan, 2006). Parameters of the jaw crusher utilised at the plant operations are shown in Table 1.

Table 1. Jaw crusher parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Close side setting (CS), mm</td>
<td>120</td>
</tr>
<tr>
<td>Open side setting (OS), mm</td>
<td>247</td>
</tr>
<tr>
<td>Throw (TH), mm</td>
<td>127</td>
</tr>
<tr>
<td>Motor (kW)</td>
<td>110</td>
</tr>
</tbody>
</table>

Rod mills are generally placed between crushing equipment and ball mill (Duroudier, 2016). Yield of the rod mill at the plant is lower compared to ball mill, whereas the motor capacity is double as the energy consumption of the rod mill is higher compared to the ball mill. Table 2 shows the plant rod mill parameters.

Table 2. Rod mill parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size, mm</td>
<td>D 2440 x L 2660</td>
</tr>
<tr>
<td>RPM</td>
<td>21</td>
</tr>
<tr>
<td>Motor size (kW)</td>
<td>250</td>
</tr>
<tr>
<td>Rod addition</td>
<td>26 Mton</td>
</tr>
<tr>
<td>RPM</td>
<td>19</td>
</tr>
<tr>
<td>Discharge slurry % solids</td>
<td>60</td>
</tr>
</tbody>
</table>

As with the rod mill, ball mills reduce size of fed ore particles by impact and attrition during dropping of the steel media near the top of the rotating cylindrical shell (Neikov et al, 2019). Parameters of the ball mill are presented in Table 3.

Table 3. Ball mill parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size, mm</td>
<td>D 2130 x L 2330</td>
</tr>
<tr>
<td>RPM</td>
<td>14</td>
</tr>
<tr>
<td>Motor size (kW)</td>
<td>125</td>
</tr>
<tr>
<td>Ball addition</td>
<td>11 Mton</td>
</tr>
<tr>
<td>RPM</td>
<td>21</td>
</tr>
<tr>
<td>Discharge slurry % solids</td>
<td>65</td>
</tr>
</tbody>
</table>

All software model inputs were established by using the actual plant equipment characteristics. For the scope of this paper, only the jaw crusher and grinding mills parameters are presented.

Modelling work

During the process simulation work mathematical equations are employed to model the plant processing streams. Modelling the complex particle size distribution (PSD) of plant circuits provides advantage on making accurate decisions and facilitates understanding of the process (Barlett, 1987).

Each equipment of the plant was presented on the METSIM flowsheet. Crushing and grinding circuit flowsheets prepared on METSIM are shown on Figure 4 and Figure 5.

Jaw crusher modelling was completed by using the METSIM jaw crushing empirical calculation option.

Software empirical calculation uses the US Bureau of Mines (USBM) method to estimate crusher product size distribution.

Screen size analysis of crushed material uses the following equation:

\[ SS = A + (B) (Z) + (C) (Z^2) + (D) (Z^3) \]  \hspace{1cm} (1)

Constants in the formula are presented in Table 4.

Table 4. Screen size analysis formula constants

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>71.3174</td>
<td>20.9630</td>
<td>2.34755</td>
<td>0.091640</td>
</tr>
</tbody>
</table>
\[ Z = -0.7 + \ln sr2 \text{ CS} - \ln sr2 \text{ MIC} \]  

(2)

where CS, MIC and Lnsr2 are crusher closed side setting, METSIM variable screen size fraction micron sizes and Logarithm to the base of the square root of two, respectively.

Software selection function formulation for crushed material is as follows,

\[ SF = 2 \times (\ln sr2 \text{ MIC} - \ln sr2 \text{ CS}) \]  

(3)

Crusher discharge material screen size analysis is calculated by the following formula:

\[ SSAd = (SS) \times (SF) \times (SSAf) + (SSAf) \times (1 - SF) \]  

(4)

where SSAf is screen size analysis of the feed material to the crusher.

Based on the laboratory test work ball mill and rod mill work index (W_i) were 17.08 and 16.23, respectively.

During ball mill model calculations, the bond inside length calculation option was employed. In this option, mill inside length is used as input and the software model calculates P_80.

Bond’s breakage and selection equations used throughout the modelling are as follows:

\[ B(X, Y) = \frac{1 - \exp\left[-\left(\frac{X}{Y}\right) \times BE\right]}{1 - \exp[-1]} \]  

(5)

\[ S(X) = \frac{AA[1] \times \left(\frac{X}{1000}\right) \times AA[2]}{1 + \left(\frac{X}{AA[3]}\right) \times AA[4]} \]  

(6)

Coefficients utilised for the equations were as follows:

BE = 1.0; \hspace{0.5cm} AA[1] = 1.1; \hspace{0.5cm} AA[3] = 1600 \hspace{0.5cm} AA[2] = 0.9; \hspace{0.5cm} AA[4] = 3.0

For the rod mill modelling, calculation option employed was simulate where mill dimensions are used and P_80 was calculated.

Selection function coefficient AL and breakage function BE utilised are, 0.5 and 1, respectively.

Rod mill selection and breakage function are as follows:

\[ B(X, Y) = \frac{1 - \exp\left[-\left(\frac{X}{Y}\right) \times BE\right]}{1 - \exp[-1]} \]  

(7)

\[ S(X) = 1 - \exp\left[-\left(\frac{X}{1000}\right) \times AL\right] \]  

(8)

**Results and discussion**

The results of each stream are presented on the output particle size distribution diagrams of the software. For the scope of this paper, jaw crusher, ball and rod mill results are compared with site data. Figure 6 and Figure 7 present the particle size distribution plant streams.

Primary crusher feed site data and simulation results are presented on Figure 8.

Oversize material from single deck screen with 2 meter wide and 6 meter long with aperture size of 125 mm was fed to the jaw crusher, stream 4 on Figure 4. The feed PSD site data closely matches the simulation results.

Fig. 6. Crushing circuit PSD output

Fig. 7. Grinding circuit PSD output

Primary crusher product site data and simulation results are presented on Figure 9. Both simulation and site data had similar particle size distributions.

For the ball and rod mill products, the simulation method selected aimed to calculate P_80.

The results of the P_80 points for both ball and rod mill simulation discharge streams were closely matched with the site data. Data for ball mill feed are presented in Figure 10.

During building of the model, the dimensions of the mills were readily available and one of the aims of this simulation study was defining P_80 point for the mill discharge.

For that reason, bond inside length calculation option for ball mill and simulate options for rod mill calculations were selected which required mill equipment parameters, and clearly the mill feed PSD data. By using these two input groups and calculation methods, simulation model gave the P_80 of the mills’ discharge streams.

For a more detailed mill discharge PSD curve that would closely match the sampled site data rod mill parameterise option is recommended to be selected by entering breakage and selectivity function coefficients to the software.

On the ball mill simulation side, selection and breakage functions coefficients could have been improved in order to calculate a complete PSD curve, if the PSD data of the plant streams was readily available at the time of the simulation model was built.

As a summary, the software was only assigned to calculate the P_80 of the mill discharge since the model built was completed at pre-operation period. The resulting P_80 values obtained from the model were close to the actual site data.

Figure 11, Figure 12 and Figure 13 present the ball mill
Fig. 8. Jaw crusher feed PSD site data vs. simulation results

Fig. 9. Jaw crusher product site data vs. simulation

Fig. 10. Ball mill feed site data vs. simulation

Fig. 11. Ball mill product site data vs. simulation

Fig. 12. Rod mill feed site data vs. simulation

Fig. 13. Rod mill product site data vs. simulation

Compliance of ethical standards
Author declares that there is no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References
ABSTRACT. Until recently, the European Union's energy policy was against coal for pollution reasons, but with the start of the military war between Russia and Ukraine, coal has become one of the energy resources to reconsider. The lack or depletion of oil and natural gas from Russia has made the coal resource the most important source and means to provide energy security. Because there are many coal-fired power stations in Romania (hard coal and lignite), its extraction and recovery becomes a real problem of national security, because it produces electricity, which is vital to Romanian society. The need to analyse the mining subsector, which generates critical mining infrastructure, comes in the context in which the possible occurrence of cases of non-energy supply, or unexpected price increases, generates major issues of national interest, with European and OTAN implications. The aim of the paper is to structure and analyse the mining subsector within the National Energy Sector in the context of stability and increasing national energy security. The authors consider that the approach of the mining subsector is a strictly national security issue because the lack of coal can cause damage to the power sector and the national economy, which are partly dependent on the mining subsector.

Key words: coal, mining subsector, national energy sector, energy security

Energy security issues

The energy security of a state represents (Băhnăreanu, 2008):
- existence, accessibility and supply of finite resources of raw materials (oil, natural gas, coal, hydrocarbons, uranium, etc.) and renewable, sufficient and available;
- clear and stable international / European trade agreements on access to these finite (re)sources of imported raw materials;
- price stability of these finite raw material (re)sources;
- control of transmission and distribution routes and alternatives to finite (re)sources of raw materials;
- the safety and security of the transformation of these finite (re)sources of raw materials into electricity;
- clear and stable trade agreements on trade in electricity with neighboring countries or those of the European Union;
- electricity price stability;
- control of electricity transmission and distribution routes;
- accessibility of each consumer (domestic / industrial) to electricity.

The level of security of a state is given by the ability of that state to aggregate resources internally, to gain and maintain access to external economic resources, and any longer interruption of energy supply has a negative effect on economic growth, political stability and welfare of the citizens of a state (Baumann, 2008).

Energy security plays a very important role in the economic security of a state, for this reason it must be taken in the most serious way, and the failure to attach importance to energy security can cause catastrophic damage with insecurity and instability, endangering the welfare of the people (Ciuta, 2010).

Structure of the national energy sector

The National Energy Sector is composed of the following subsectors: (Figure 1) (Fiță, 2021a).
- Oil subsector:
  - Oil Branch;
  - Natural Gas Branch.
- Nuclear Subsector - Uranium;
- Mining Subsector - Coal;
- Electrical energetic subsector – Electricity.
Mining subsector - coal

Generalities regarding the Romanian mining industry

Coal continues to be an important source of energy that can maintain its role as a safe fuel, for many countries being the only fuel available to meet the growing demand for electricity needed to raise living standards. It is very possible that this solid fuel will maintain its share in the global primary energy demand, which is transformed into electricity by using it in thermal power plants.

Romania has almost 200 years of experience in the coal mining industry, and the main national actors in coal mining and extraction are the following:

- Jiu Valley Mining Basin (hard coal – high calorific value coal):
  - Lonea Mine;
  - Livezeni Mine;
  - Vulcan Mine;
  - Lupeni Mine.
- Oltenia Mining Basin (lignite - lower calorific value coal):
  - Roșia – Rovinari open-pit mine;
  - Jilț open-pit mine;
  - Motru open-pit mine.

The operating principle of the mining subsector is shown in Figure 2 (Fîță, 2021b).

The complete mining cycle in Romania

Romania currently has rich coal resources (hardcoal and lignite), but the major advantage is that there is a complete mining cycle in the country (Table 1 and Figure 3).

Table 1. Synthesis of the complete mining cycle in Romania

<table>
<thead>
<tr>
<th>Crt. no.</th>
<th>Stages</th>
<th>Resource type</th>
<th>Operator</th>
<th>Secondary operator</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Resource Management</td>
<td>hardcoal / lignite</td>
<td>National Agency for Mineral Resources</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Mining/Processing/Transportation</td>
<td>hardcoal</td>
<td>Hunedoara Energy Complex</td>
<td>Lonea, Livezeni, Vulcan, Lupeni Mines</td>
</tr>
<tr>
<td></td>
<td></td>
<td>lignite</td>
<td>Oltenia Energy Complex</td>
<td>Roșia - Rovinari, Jilț, Motru Mines</td>
</tr>
<tr>
<td>3.</td>
<td>Electricity generation</td>
<td>hardcoal</td>
<td>Hunedoara Energy Complex</td>
<td>Deva, Paroșeni</td>
</tr>
<tr>
<td></td>
<td></td>
<td>lignite</td>
<td>Oltenia Energy Complex</td>
<td>Craiova II Thermal Power Stations</td>
</tr>
</tbody>
</table>

In order for the mining cycle to be complete through the 3 stages, it is mandatory that all the 3 actors involved are present, namely: (Figure 3) (Fîță, 2021c)

1) National Agency for Mineral Resources - which owns the coal resource (hardcoal and lignite);
2) Hunedoara Energy Complex/Jiu Valley Mine Closing - which exploits, processes, transports and produces hardcoal-fired electricity;
3) Oltenia Energy Complex – which exploits, processes, transports and produces lignite-fired electricity.

The National Mining System – mining operations

1. Hunedoara Energy Complex:
   - geological research for the discovery of coal reserves;
   - production, supply and marketing of hardcoal-fired electricity;
   - production, dispatching, transport, distribution and supply of thermal energy.

2. Jiu Valley Mine Closing:
   - hardcoal extraction;
   - mine closing and restoration of affected areas.

3. Oltenia Energy Complex:
   - lignite extraction and processing;
   - lignite-based electricity and heat generation (Fîță, 2021c)

Fig. 2. The operating principle of the mining subsector

Fig. 3. Scheme of the complete mining cycle in Romania
3.4. The mining pressure tool

Definition: Any action or inaction of an actor in the mining energy chain RESOURCE HOLDER (hardcoal / lignite coal) – MINE OPERATOR / PREPARATOR / RESOURCE TRANSPORTER (hardcoal / lignite coal) - ELECTRICITY MANUFACTURER (based on coal or lignite) directly connected to hard coal or lignite resources, which aims to influence the behaviour of other actors, to control or eliminate them, in order to achieve their own interests.

The principle diagram of the use of coal energy resources (hardcoal / lignite) as a pressure tool is shown in Figure 4 (Fîță, 2021b, c).

Fig. 4. Schematic diagram of the use of mining energy resources - hardcoal and lignite - as a pressure tool

The pressure tool can be used throughout the chain by any of the "links" involved in this process.

Conclusions

Because coal resources (hardcoal and lignite) are elements of safety and security for those who own them, they can lead to conflicts or energy wars, which are characterised by the use of energy tools to force the opponent to change his policy or behaviour and it undermines the ability of that state to maintain normal relations with other states, in time of peace or war. Without coal resources (hardcoal and lignite), the national economy could suffer as thermoelectric power production is halted, causing huge damage to national industry and energy security, and energy security is becoming an important component of the national security and external politics. Coal resources can be used as tools of political pressure or energy weapon for profit or economical / political pressure.

The only drawback of coal is air pollution, except gasification, but the costs are enormous. That is why the European Union is against it, but it must be taken into account that it ensures energy security and stability, which is why it is vital.

References


STUDY ON THE FERRIC IRON ADSORPTION FROM ACID MINE DRAINAGE ON LEWATIT RESIN IN A FIXED-BED COLUMN

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ABSTRACT. The study aimed to determine the effect of the acid mine drainages’ flow rate on the iron adsorption by ion-exchange resin LEWATIT MonoPlus TP 207 in a fixed-bed column and to evaluate which widely used models describe that process better. The ferrous iron was preliminary chemically oxidised by H₂O₂ and Na₂S₂O₃ addition and increased pH to 3.50 combined with the solution purging with air. After assembling fixed-bed columns, their bed volume (BV) was determined. The treated mining solution was delivered to fixed-bed columns by a peristaltic pump at 2.0, 3.0, and 4.0 BV flow rates. The iron adsorption efficiency on the LEWATIT resin was studied depending on the applied flow rate and the volume being treated. The experimental data obtained were modelled using the Bohart-Adams, Thomas, Yoon-Nelson, and Clark models. The results showed that at constant experimental conditions (temperature, ferric iron concentration, and pH), the applied flow rate had a significant effect on the parameters which are important from a practical (efficiency of iron removal (γ); equilibrium iron and equilibrium copper contents of the resin, (qeq)); and a theoretical point of view (rate constants (ka, kb, kN, kr); time of breakthrough (τ)). The Yoon-Nelson and Clark models were the models that best fitted the experimental results.

Keywords: iron, LEWATIT, adsorption, a fixed-bed column

Introduction

The hydrometallurgical processing of non-ferrous metals from raw materials usually relies on their leaching at a highly acidic pH, combined with the co-dissolution of a significant amount of iron. For that reason, iron removal is an obligatory preliminary step in the treatment/processing of wastewater and laden leach solution from mining and metallurgical industries. Solvent extraction and ion exchange are the processes, and they are applied in two consecutive stages. The first stage is the selective removal of ferric iron and its concentration on the reagent surface. The organo-phosphorous acids are the main class of organic compounds used in solvent extraction. Their advantage is the selective extraction and a strong bond formation with ferric iron from the leach liquor (Azizorghaben et al., 2016). An approach similar to the above-mentioned is based on the operation of ion-exchange resins. They are prepared from a wide range of synthetic polymers, and each class is characterised by a specific surface group and a magnitude of surface charge. Therefore, it determines the resins’ ability to extract selectively alkaline earth elements, non-ferrous metals or precious metals even from solutions with higher inorganic or organic compounds with excellent complexing properties. For that reason, the ion exchange resins are used not only for the processing of mining effluents and laden leach liquor from metallurgy (McKevitt and Dreisinger, 2009) but also for the final purification as a step in the secondary treatment of wastewater from the food industry (Victor-Ortega et al., 2016). LEWATIT ion exchange resins are commercial products widely used in practice for dealkalisation, softening, demineralisation of natural and industrial waters, catalysis and processing of different organic compounds to produce foods or biodiesel (Product Guide, 2021). Another study showed that the loading capacity of LEWATIT ion exchange resin to iron is equal to or higher than that of other ion-exchange resins applied at an industrial scale (McKevitt and Dreisinger, 2009).

The second stage of the laden leach liquors processing is the regeneration of the relevant active surface, and it is achieved in the presence of a suitable inorganic acid. As a result, the extracted and concentrated amount of ferric iron is desorbed in a solution with higher purity and a volume considerably lower than the initial volume of the laden leach liquor (Azizorghaben et al., 2016). It enables further iron precipitation of hematite or magnetite with higher chemical purity, peculiar particle size, shape, surface, optical and magnetic properties which make them applicable in various industrial fields (Kulkarni et al., 2014).

The study aimed to determine the effect of the acid mine drainages’ flow rate on the iron adsorption by LEWATIT MonoPlus TP 207 in a fixed-bed column and to evaluate which widely used models describe that process better.

Materials and methods

Acid mine drainage (AMD) from an abandoned copper mine in Northwest Bulgaria with acidic pH (2.26) was collected and analysed. The iron, copper, and zinc content was 3345, 137, and 311 mg/L, respectively. The value of Eh shows that a significant part of the dissolved iron was a ferrous iron (Georgiev et al., 2021).

The experiments about the iron adsorption from acid mine drainage were carried out in fixed-bed columns with a total length of 10 cm. The experimental set-up consisted of a feed vessel (1), a peristaltic pump (2), a fixed-bed column (3), and a vessel collecting treated solutions (4) (Figure 1). In each fixed-bed column, two zones were distinguished – an adsorption and a supporting zone. The adsorption zone occupied the central part of the column, and it consisted of LEWATIT MonoPlus TP 207 ion-exchange resin (mean bead size 0.61 (± 0.05) mm). The supporting zones, situated in each column’s inlet and outlet point, consisted of glass wool. The working volume of the adsorption zone, the so-called bed volume (BV), was determined by an upward injection of water at a rate of 0.048 m³/h till all pores existing between the resin’s beans filled up with water. Initially, the ion exchange resin in a fixed bed column was activated with an upward injection of 0.1 L solution containing 100 g/ L sulphuric acid by a peristaltic pump at
0.096 L/h (Table 1). After that, the resin was washed with 0.240 L tap water at the same injection rate to extract the non-consumed acid from the exchange resin.

The ferrous iron in the collected AMD oxidised chemically in advance by H₂O₂ and Na₂CO₃ addition to pH 3.50 and purging with air which led to the formation of voluminous precipitates of ferric hydroxides with orange colour. The pulp was injected into the fixed-bed columns upward by a peristaltic pump, Ismatec, at flow rates of 0.096, 0.144, or 0.192 L/h, respectively. The temperature during the experiments was constant (25°C). The effluents from each fixed-bed column were collected separately and stored in a refrigerator until the chemical analysis. pH, iron and copper concentration were determined by its selective complexation with copper ammonia method (oc et al., 2003; Malk Nelson, 1984), and Clark (Clark, 1987) models were used for kinetic studies of the iron adsorption on LEWATIT resin in a fixed-bed column. According to the Bohart-Adams model, the following equation describes the iron content in effluents of a fixed-bed column:

\[
\ln \left( \frac{C_i}{C} \right) = \left( -\frac{k_{BA} N_i \tau}{\nu} \right) + \left( k_{BA} C_i \cdot t \right)
\]

where: k_{BA} is the Bohart-Adams rate constant [L / (mg · min)], N_i is the saturation concentration (mg/L), \( \nu \) is the linear velocity of AMD injection to a fixed-bed column (cm/min), \( Z \) is the bed depth (cm). The k_{BA} and N_i were determined from the intercept and slope of the linear plot of \( \ln \left( \frac{C_i}{C} \right) \) against time (t), respectively.

The Thomas model is given in linear form by the following expression:

\[
\ln \left( \frac{C_i}{C} - 1 \right) = \left( k_T \cdot q_{max} \cdot m \right) / Q - \left( k_T \cdot C_i \cdot t \right)
\]

where k_T is the Thomas rate constant [L / (mg · min)], \( q_{max} \) is the maximum iron (mg/g), and m is the mass of sorbent resin in a fixed-bed column (g), \( Q \) is the volumetric flowrate of AMD (L/min). The parameters k_T and \( q_{max} \) were determined from the intercept and slope of the linear plot of \( \ln \left( \frac{C_i}{C} - 1 \right) \) against time (t), respectively.

The Yoon-Nelson model is given in a linear form by the expression:

\[
\ln \left( \frac{C_i}{C} - C_o \right) = (k_{YN} \cdot t) - (r \cdot k_{YN})
\]

where \( k_{YN} \) is the Yoon-Nelson rate constant (min⁻¹), \( r \) is the time required for 50 % iron breakthrough (min). The parameters \( r \) and \( k_{YN} \) were determined from the intercept and slope of the linear plot of \( \ln \left( \frac{C_i}{C} - C_o \right) \) against time (t), respectively.

The kinetic studies for evaluation of the iron breakthrough curves in fixed-bed columns

Bohart-Adams (Bohart and Adams, 1920; Qureshi et al., 2011), Thomas (Thomas, 1944), Yoon-Nelson (Yoon and Nelson, 1984), and Clark (Clark, 1987) models were used for kinetic studies of the iron adsorption on LEWATIT resin in a fixed-bed column. The effect of the applied flow rate and the volume solutions injected into the columns on the iron adsorption by iron exchange resin LEWATIT MonoPlus TP 207 was studied by the breakthrough curves construction (function C_e / C_i of time).
in a batch regime, \( r \) is the Clark rate constant (min\(^{-1}\)), and \( A \) is the Clark model constant. The parameters \( r \) and \( A \) were determined from the intercept and slope of the linear plot of \( \ln [(C_s/C)^{1.5}] \) against time \( (t) \), respectively. The values of saturation concentration, \( N_0 \) and \( q_{\text{max}} \) were calculated according to Rocha et al. (2015):

\[
N_0 = C_s.v.\ln A/ Z.r \quad (13)
\]

\[
q_{\text{max}} = N_0 \cdot BH \quad (14)
\]

where \( BH \) is the Bed volume/height of the adsorption zone in the fixed-bed column, \( \text{cm}^3/\text{cm} \).

The regression coefficient \( (R^2) \) was used to evaluate the fitting of the experimental data to the linearised forms of the applied models.

Table 1. Characteristics of the fixed bed-columns experiment about the effect of flow rate on the Fe\(^{3+}\) adsorption on ion-exchange resin LEWATIT MonoPlus TP 207

<table>
<thead>
<tr>
<th>Index</th>
<th>Applied flow rate, BV/h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>Bed volume of the fixed-bed column, cm(^3)</td>
<td>48</td>
</tr>
<tr>
<td>Bed height in the fixed-bed column, cm</td>
<td>62.3</td>
</tr>
<tr>
<td>Bed volume/height of adsorption zone, BH, cm(^3)/cm</td>
<td>3345</td>
</tr>
<tr>
<td>Mass of the resin in the column, m</td>
<td>0.096</td>
</tr>
<tr>
<td>Fe in AMD, mg/L</td>
<td>0.166</td>
</tr>
<tr>
<td>Flow rate, L/h</td>
<td>2.0</td>
</tr>
<tr>
<td>The linear velocity of the solution, cm/min</td>
<td>6.0</td>
</tr>
</tbody>
</table>

Results and discussion

The volume of acid mine drainage generated at the mine sites varies quite a lot seasonally. The highest volume of mining effluents is detected in spring and autumn when the maximum annual precipitation is, opposite to summer when the minimum is. Therefore, the volume of generated acid mine drainage from mines had an opposite effect on the concentration of iron and non-ferrous metals being measured (Groudev et al., 2008). For that reason, the value of flow rate applied during the treatment of acid mine drainage, both by active and passive technologies, had a significant effect on the process efficiency. Three different flow rates of acid mine drainage with constant composition were applied to the fixed-bed columns to reveal that effect. The bed volume (BV) value determined the actual values of flow rates to the fixed-bed columns used in that study. The bed volume presents the total volume of pores between the resin beads, and its values in all columns were 48 mL (Table 1). The studied flow rates were 2.0, 3.0, and 4.0 BV, corresponding to 0.096, 0.144, and 0.192 L/h of acid mine drainage applied to the fixed-bed columns. The previous study (Georgiev et al., 2021) showed that the resin adsorbed the ferric iron preferentially when preliminary neutralised acid mine drainage to a pH of 3.50 is used. It enhanced ferrous to ferric iron oxidation in the presence of \( \text{H}_2\text{O}_2 \) and an excess of oxygen by air purging and iron hydrolysis and precipitation to goethite. The acid mine drainage treated in that way was delivered to the fixed-bed columns upward. As a result, the solution filled up completely the column’s bed volume, and cations took part in the ion-exchange processes with the protonated surface of the resin. As a result, the excess protons were transferred from the resin surface to the solution. Goethite dissolution was enhanced, ferric iron release to solutions, and its sorption on the resin surface. For that reason, apart from the iron and copper concentrations, the pH of effluents from each column was measured regularly (Table 2). The results revealed that the amount of ferric iron adsorbed on the resin surface was higher, while the pH of the columns effluents was lower. For example, pH and ferric iron concentrations in effluents at 2 hours since the start of the experiment were 1.23 and 141.6 mg/L, respectively, when the applied flow rate was 2 BV. However, when the applied flow rate was 4.0 BV, the iron sorption

Table 2. Characteristics of the fixed bed columns effluents depending on the applied flow rate

<table>
<thead>
<tr>
<th>Index</th>
<th>Applied flow rate, BV/h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>Reached at time, hour</td>
<td>2.0</td>
</tr>
<tr>
<td>pH</td>
<td>1.23</td>
</tr>
<tr>
<td>Fe, mg/L</td>
<td>141.6</td>
</tr>
<tr>
<td>Cu, mg/L</td>
<td>12.6</td>
</tr>
<tr>
<td>Reached at time, hour</td>
<td>4.0</td>
</tr>
<tr>
<td>pH</td>
<td>1.67</td>
</tr>
<tr>
<td>Fe, mg/L</td>
<td>2170</td>
</tr>
<tr>
<td>Cu, mg/L</td>
<td>176.4</td>
</tr>
<tr>
<td>Reached at time, hour</td>
<td>6.0</td>
</tr>
<tr>
<td>pH</td>
<td>1.89</td>
</tr>
<tr>
<td>Fe, mg/L</td>
<td>3345</td>
</tr>
<tr>
<td>Cu, mg/L</td>
<td>164.3</td>
</tr>
</tbody>
</table>

Fig. 2. Breakthrough curves for Fe\(^{3+}\) adsorption on ion-exchange resin LEWATIT MonoPlus TP 207 at the studied flow rate
at 2.0, 3.0, and 4.0 BV were at 0.384, 0.576, and 0.768 L, respectively (Table 3). After the end of each fixed-bed column’s operation, the experiments showed that the equilibrium iron content on the resin ($q_{\text{eqFe}}$) gradually decreased from 15.0 mg/g to 13.3 when the flow rate increased from 2.0 to 4.0 BV (Table 3). In the same order, the efficiency of iron sorption gradually decreased from 72.7% to 32.4% when the relevant volume of acid mine water passed through the fixed-bed columns. The lower values of equilibrium iron content on the resin was reported by other authors in the experiments when the inlet iron concentration to the fixed-bed columns decreased significantly (Millar et al., 2015; Victor-Ortega et al., 2016). The higher flow rates also had a negative effect on the values of the equilibrium content of copper on the resin ($q_{\text{eqCu}}$) and the ratio between equilibrium iron to copper content ($q_{\text{eqFe}} / q_{\text{eqCu}}$). Therefore, some limitations could arise in applying iron oxides produced during the further processing of the iron-loaded ion exchange resin (Georgiev et al., 2020).

Table 3. Parameters characterising the ferric iron adsorption on the ion-exchange resin LEWATIT MonoPlus TP 207 in a fixed bed-column

<table>
<thead>
<tr>
<th>Index</th>
<th>Applied flow rate, BV/h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
</tr>
<tr>
<td>Amount of solution passed through the column, $V_{\text{ret}}$, L</td>
<td>0.384</td>
</tr>
<tr>
<td></td>
<td>0.576</td>
</tr>
<tr>
<td></td>
<td>0.768</td>
</tr>
<tr>
<td>The total amount of ferric iron delivered to the fixed-bed column, $m_{\text{total}, \text{mg}}$</td>
<td>1285</td>
</tr>
<tr>
<td></td>
<td>1927</td>
</tr>
<tr>
<td></td>
<td>2569</td>
</tr>
<tr>
<td>The total amount of adsorbed iron, $q_{\text{Fe}}$, mg</td>
<td>934.5</td>
</tr>
<tr>
<td></td>
<td>913.1</td>
</tr>
<tr>
<td></td>
<td>831.9</td>
</tr>
<tr>
<td>The efficiency of the ferric iron adsorption, Y, %</td>
<td>72.7</td>
</tr>
<tr>
<td></td>
<td>47.4</td>
</tr>
<tr>
<td></td>
<td>32.4</td>
</tr>
<tr>
<td>Equilibrium amount of adsorbed iron, $q_{\text{eqFe}}$, mg/g</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>14.6</td>
</tr>
<tr>
<td></td>
<td>13.3</td>
</tr>
<tr>
<td>Equilibrium amount of adsorbed copper, $q_{\text{eqCu}}$, mg/g</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>0.56</td>
</tr>
<tr>
<td>Time of 50 % iron breakthrough concentration, hours</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>1.75</td>
</tr>
<tr>
<td>The ratio of $q_{\text{eqFe}} / q_{\text{eqCu}}$</td>
<td>31.9</td>
</tr>
<tr>
<td></td>
<td>28.7</td>
</tr>
<tr>
<td></td>
<td>23.8</td>
</tr>
</tbody>
</table>

Fig. 3. Bohart-Adams model for the Fe$^{3+}$ adsorption on the ion-exchange resin LEWATIT MonoPlus TP 207 at the studied flow rate

The sorption processes carried out in fixed-bed columns are described by different mathematical models (Kundu and Gupta, 2005). These models are organised on the fraction of sorption capacity remaining free, model type followed during the adsorbate sorption, or the order of equation rate. For that reason, there is no universal model applicable for modelling the sorption regardless of the type of studied adsorbate or used adsorbent.

The Bohart-Adams model is based on the surface reaction theory, according to which the rate of adsorption is proportional to the fraction of free adsorption capacity that still exists on the adsorbent surface (Bohart and Adams, 1920). That model was used to assess adsorbate removal by ion-exchange resins (Al-Sheikh et al., 2020). The results about the iron adsorption on the resin showed that the values of the linear velocity of solution through the fixed bed column, which was dependent on the applied flow rate, had a significant effect on the values of the Bohart-Adams rate constant ($k_{BA}$) and the saturation concentration ($N_0$), respectively (Table 4). For example, when the flow rate changed from 2.0 to 4.0 BV, the values of $N_0$ steadily increased and reached 18677 mg/L at the highest applied flow rate. Meantime, the $k_{BA}$ values decreased due to the higher linear solution’s velocity passing through the resin bed in the column and the lower contact time for the ferric iron adsorption. For that reason, 13.3 mg Fe/g resin was the lowest value of the equilibrium iron content ($q_{\text{eq}}$) among the tested flow rates, determined experimentally at the study’s end (Table 3). However, experimental fixed bed-column results fit well with the Bohart-Adams model when more than 50 % of binding sites of adsorbents are still unoccupied (Figure 3). For that reason, the Bohart-Adams model was not suitable for modelling iron adsorption from mining effluents, mainly when the fixed-bed column operates at higher flow rates.

Previous batch experiments revealed that ferric iron adsorption on LEWATIT resin followed second-order kinetics (Georgiev et al., 2021). The Thomas model follows the same kinetics, and it was included in the assessing tool for evaluating the experimental data for that reason (Thomas, 1944) – Figure 4. The main advantage of the Thomas model is the determination of the maximum adsorbate content ($q_{\text{max}}$) retained on the adsorbent surface in a dynamic regime of operation.

Fig. 4. Thomas model for Fe$^{3+}$ adsorption on the ion-exchange resin LEWATIT MonoPlus TP 207 at the studied flow rate

The values of $q_{\text{max}}$ of iron adsorbed on the resin strongly depended on the applied flow rate of acid mine drainage to the column and Thomas rate constant ($k_{TH}$) (Table 4). For example, 2.0 BV used flow rate determined the highest values of $q_{\text{max}}$ (18.2 mg/g) on the ion exchange resin LEWATIT MonoPlus TP 207 (Table 4). However, the values of maximum iron content retained by the resin at all studied flow rates were higher than the equilibrium iron content ($q_0$) determined experimentally at the end experiment (Table 3) and the maximum iron content ($q_{\text{max}}$) defined in a batch regime of operation (Georgiev et al., 2021). This discrepancy could be explained in two ways. Firstly, it is a well-known weakness that
the Thomas model overestimates the experimental values of the maximum adsorption capacity of adsorbents (Victor-Ortega et al., 2016; Negrea et al., 2020). Secondly, the acid mine drainage used in experiments contained 137 mg/L Cu\(^{2+}\) too, and despite ferric iron's preferential adsorption instead of copper (McKevitt and Dreisinger, 2009; Product Guide, 2021), some amount of it was also adsorbed (Table 3). As a result, it has a negative effect on the ferric iron content adsorbed by the ion exchange resin.

The main advantages of the Yoon-Nelson model (Yoon and Nelson, 1984) in comparison to the other models used in the study are fewer parameters needed for the model application and calculation of the time required for 50% of adsorbate breakthrough ($\tau$). The data presented in Table 4 revealed that the values of $r$ had a tendency for steady decrease when higher flow rates of acid mine drainage to the fixed bed columns were applied.

**Table 4. Ferric iron adsorption parameters on the ion-exchange resin LEWATIT MonoPlus TP 207 calculated by the applied models**

<table>
<thead>
<tr>
<th>Model</th>
<th>Flow rate, BV/h</th>
<th>Column adsorption parameters</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bohart-Adams</td>
<td>$k_B$, L mg(^{-1}) min(^{-1})</td>
<td>$N_0$, mg/L</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>8.97.10(^4)</td>
<td>13025</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>7.47.10(^4)</td>
<td>18145</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>2.99.10(^4)</td>
<td>18677</td>
</tr>
<tr>
<td>Thomas</td>
<td>$k_{th}$ (L mg(^{-1}) min(^{-1}))</td>
<td>$q_{max}$, mg/g</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>1.14.10(^4)</td>
<td>18.2</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>1.23.10(^4)</td>
<td>16.9</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>9.27.10(^4)</td>
<td>16.3</td>
</tr>
<tr>
<td>Yoon-Nelson</td>
<td>$k_{YN}$, (min(^{-1}))</td>
<td>$\tau$, (min)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>0.038</td>
<td>211.8</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>0.043</td>
<td>153.5</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>0.031</td>
<td>97.7</td>
</tr>
<tr>
<td>Clark</td>
<td>$N_0$, mg/L</td>
<td>$q_{max}$, mg/g</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>199.9</td>
<td>16.1</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>189.4</td>
<td>15.2</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>170.7</td>
<td>13.7</td>
</tr>
</tbody>
</table>

**Fig. 5. Yoon-Nelson model for the Fe\(^{3+}\) adsorption on the ion-exchange resin LEWATIT MonoPlus TP 207 at the studied flow rate**

Furthermore, the predicted times were very similar to the times determined during the monitoring of the fixed-bed column operation (Table 3). Figure 5 also shows that theoretical results fitted very well with the experimental ones depicted by the linear form of the model. For that reason, the Yoon-Nelson model could be used in other studies regarding raw components removal from laden leach solutions by ion-exchange resins.

The Clark model was the last model applied to the experimental results. It is based on the assumption that adsorbate sorption follows the Freundlich isotherm (Clark, 1987). 1.909 was the value of the Freundlich constant $n$ used to calculate the Clark parameters ($r$ and lnA) in the model. The values of both parameters decreased when higher flow rates were applied to the fixed-bed columns (data not shown). However, the values of correlation coefficients were higher than 0.99, which showed a good agreement between the model and the experimental results (Table 4, Figure 6).

**Conclusions**

At constant experimental conditions (temperature, ferric iron concentration, and pH), the applied flow rate significantly affected equilibrium iron content, $q_{eqFe}$, on the ion-exchange resin LEWATIT MonoPlus TP 207. Its highest value was 15.0 mg/g when the applied flow rate to a fixed-bed column was 2 BV. However, when the fixed-bed column operated at higher flow rates, $q_{eqFe}$ decreased gradually. It resulted from a lower percentage of iron removal, considering the total amount of iron delivered and worse ratio values between the equilibrium content of iron and copper on the resin.

The Yoon-Nelson and the Clark model better described ferric iron sorption on ion-exchange resin LEWATIT MonoPlus TP 207 than the other applied models (i.e. Bohart-Adams and Thomas models) and they could be used further in studies about the processing of rich-in-iron mining effluents with ion-exchange resins.

The Yoon-Nelson and the Clark rate constants of the models mentioned above are good tools to assess the effect of the flow rate on ferric iron sorption on the ion-exchange resin LEWATIT MonoPlus TP 207 in fixed-bed column studies.
Acknowledgements.

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BRINGING SPACE TECHNOLOGY TO MINING – BIOSENSORS FOR HEALTH MONITORING IN REAL TIME AS A MODERN MANAGEMENT PRACTICE

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ABSTRACT. Nowadays, mining industry is striving to be regarded as a modern and highly-technological field with no negative connotation to its name. The human factor is constantly increasing in significance, making mining industry more people oriented, and more and more efforts are being made to bring modern technologies into service and help create safer work environment. Utilising new types of biosensors provides remote health monitoring of workers in mining industry, thus enabling the real time monitoring of vitals of a person, permitting timely medical care and preventing long-term negative exposures. In this regard, the use of flexible, lightweight and wearable biosensors is seen as very convenient and patient-friendly in work environment without interfering with the daily activities. In this study we present a non-enzymatic glucose sensors based on ZnO nanoparticles prepared by a laser ablation in liquid method.

Key words: ZnO nanoparticles, laser ablation, biosensors, glucose

Introduction

Over the last decade, mining industry has been constantly developing in terms of engaging new technologies in the field. Different approaches employing non-conventional eco-friendly techniques such as phytomining and unmanned aerial systems are gradually being utilised to replace traditional mining processes. At the same time, the importance of the human factor is constantly increasing and companies around the world are now investing in creating a safe work environment with the aid of the latest technology achievements.

Space programmes were always the driving force for the development of cutting-edge technologies. The concept of “lab-on-chip” devices is a prime candidate for the use in space missions due to the specific requirements for such tasks (small volume, lightweight, as well as low sample and reagent consumption). Designing a “true” lab-on-chip system requires integration in a single device of sample handling, analytical detection and signal transduction that would permit remote monitoring and analysis.

As an example, chemiluminescence (CL) was proposed as a detection method for chemical and biological samples (Nascetti, 2016) since it does not require excitation source which makes it suitable for miniaturised devices. Based on this study, as well as on similarities in work environment (such as hazardous and remote location with the lack of immediate medical assistance), we considered the implementation of small and wearable devices (Yang and Cheng, 2020) that can monitor the health of mine workers in real time underground. For this purpose, the so-called biosensors could be very promising candidates, that is, devices that respond to some biological or chemical reactions by producing a signal proportional to the concentration of the target analyte in the reaction.

A biosensor usually incorporates five parts: (i) an analyte (a substance, usually a biological molecule whose concentration is to be monitored, e.g. glucose); (ii) a bioreceptor (an agent that specifically recognises the analyte and generates a signal, such as light, heat, pH, charge, or mass change, etc., the so called bio-recognition); (iii) a transducer (which converts the generated signal into either optical or electrical signals proportional to the analyte concentration); (iv) electronics (which consists of complex electronic circuitry that converts the signal to digital form); and (v) a display (which is either a computer or a printer that displays numbers and results (Bhalla, 2016)).

Biosensors can be successfully utilised in some disease monitoring, drug discovery, detection of pollutants or disease-causing micro-organisms and markers that are indicators of a disease in bodily fluids (blood, urine, saliva, sweat, see: Bhalla et al., 2016). Different detection methods were reported, with those based on electrochemical technique being preferred owing to their swift response, high selectivity, high sensitivity and stability. Usually, enzymatic sensors are utilised due to their high selectivity based on biochemical reactions with a metabolite, however, they suffer from the complexity of immobilisation, the density of the enzyme layer and a relatively poor durability over time (working cycles) (Wang, 2008; Tremey et al., 2017). To overcome these obstacles, research explored the possibility of nonenzymatic glucose sensors as electrochemical biosensors (Hwang et al., 2018). Sensors of this type have low costs, relatively simple manufacturing and are stable over time (Dhara and Mahapatra, 2018). The electroactive part of nonenzymatic sensors usually involves metals, metal alloys and transition-metal oxides (because of their high catalytic activity). Electrodes can be deposited on a flexible support (for example, by electrodeposition), thus creating a sensor device that can be firmly and closely attached to a body surface and monitor analytes (glucose) in sweat over a long period of time (Li et al., 2021).

Analysis of the literature reveals that sensors proposed so far: (i) are not sensitive enough, (ii) often demonstrate low selectivity, and (iii) are not available yet as a commercial product ready to use (Bandodkar et al., 2019). That is why new approaches, as well as new materials, are actively sought these days to accelerate the field and develop wearable sensors for non-invasive detection of glucose and other biomedical applications (Mani et al., 2017).

Body sweat is an epidermal fluid containing various metabolites, electrolytes and trace elements released from the
body. In contrast to other biological fluids (such as blood, serum, plasma), sweat is excreted and can be collected non-invasively, and thus can be easily used for diagnostic tests. Numerous biomarkers available in the sweat were shown to reveal the physiological status of blood, which is why they can be a signal of our body functions and total fitness. Sweat contains numerous biomolecules, of which the most abundant are glucose and lactates. And because of the remarkable demand for the development of non-invasive health-test methods, the latter two markers are of very high research interest as analytes these days (Cho et al., 2018; Currano et al., 2018). Therefore, development of fast, flexible, wearable sensors for non-invasive sweat analysis is highly desirable for the society and is a real ‘hot topic’ nowadays.

Laser ablation in liquid (LAL) is a convenient and efficient technique to produce diverse nanoparticles (NPs) at laboratory scale (Niu et al., 2010; Zeng et al., 2012; Kondo et al., 2017; Mintcheva et al., 2018). In this approach, a laser beam is typically focused on a solid target, producing plasma, vapour or molten metal drops which then react with the liquid medium and give rise to NPs of metal oxides, sulphides or carbides. Compared with conventional chemical methods, LAL is a simple and green technique that offers facile one-step synthesis of NPs, operates in a minimum volume of liquid medium and often permits to control both chemical composition and morphology of produced NPs (Niu et al., 2010; Zeng et al.; 2012 Kondo et al., 2017; Mintcheva et al., 2018). Because of very high temperature gradients and quenching rates in the ablation zone, the method often allows for production of NPs with metastable phases and/or unique morphologies and properties, which is of direct interest for the present research as such NPs cannot be prepared by other methods (Niu et al., 2010; Zeng et al., 2012; Kondo et al., 2017; Mintcheva et al., 2018). Recently, LAL-produced nanomaterials proved to be efficient chemiresistive gas sensors at room temperature (Kondo T. et al., 2017; Mintcheva N. et al., 2018). That is why, incorporating such nanomaterials as sensing elements into wearable sensors for biomedical use looks very timely and promising.

To achieve the above challenging goal, we planned the following key progressive objectives: (i) preparation of nanomaterials via laser ablation in liquid; (ii) their separation and characterisation; (iii) fabrication of flexible and wearable sensing electrode; (iv) testing of the newly prepared sensors as detectors of glucose ions in sweat by performance of cyclic voltammetry measurements. The results of each of these stages were described and presented in this paper.

Method and Materials

Preparation of ZnO NPs.

ZnO NPs were prepared by irradiation of Zn plate (99.5% purity, 2 mm thick) with nanosecond pulsed laser (Nd: YAG) with the following parameters: 532 nm as wavelength, 10 Hz as frequency, 50 mJ/pulse and 45 min as pulse energy and ablation time, respectively. The procedure was performed using conditions previously described by Gavrilenko et al. (2019). The Zn plate was pre-treated by consecutive washing in acetone, ethanol and pure water for 180 s and then immersed in quartz cuvette (30 mm x 30 mm x 50 mm, wall thickness of 2 mm) filled with 20 ml of pure water. The obtained dispersion was centrifuged for 10 min (16,500 rpm) and the ZnO NPs were washed with pure water three times and redispersed and used for further analysis of the prepared material.

Glucose sensing measurements

To test the electrochemical activity of the obtained ZnO NPs, we used a three-electrode system (PalmSens4, potentiostat/galvanostat/impedance analyser) where ZnO NPs (deposited on glass carbon electrode, GCE) act as a working electrode (Ag/AgCl and Pt are used as a reference and a counter electrode, respectively). The ZnO NPs were applied as a thick paste (in ethanol) after sonication for 15 min at room temperature. For the electrochemical experiments, a solution of artificial sweat was prepared (from Nanochemazone, Canada and 0.1 M NaCl) and then used in all glucose sensing experiments.

Results and Discussion

The ZnO NPs prepared in pure water were separated by centrifugation, washed three times and characterised by UV-Vis spectroscopy and SEM. The spectrum of diluted dispersion of ZnO NPs taken on Shimadzu UV-2450 spectrometer is shown in Figure 1.

![Fig. 1. UV-Vis spectrum of ZnO NPs](image)

The absorption maximum observed at 345 nm is attributed to the presence of nanosized ZnO and the position of the maximum is related to the particle size (band gap energy transition).

The formation of ZnO NPs is also confirmed by SEM analysis which showed two fraction of particles, with average sizes around 150-200 nm diameter and around 50-100 nm (see Figure 2).

![Fig. 2. SEM image of ZnO NPs separated from water dispersion](image)
Since the laser-prepared ZnO NPs were free of any surfactants (because no surfactants or any reagents were used during laser ablation in water), they were expected to be suitable for the active part of biosensors due to lack of interference with the surface chemistry in redox processes.

The potential of ZnO NPs as a working electrode in glucose sensing in sweat was tested by cyclic voltammetry (CV) measurements, the results being displayed in Figure 3.

**Fig. 3.** CV curves in artificial sweat solution (0.1 M NaCl) with different concentration of glucose (2; 4; 6; 8 and 10 mM) recorded for working electrode modified with ZnO NPs.

Direct electrochemistry of the electrode (modified with ZnO NPs) in artificial sweat revealed a pair of well-defined redox peaks which are characteristic for glucose. Their intensity is seen to change with the concentration of glucose, which shows good catalytic activity for glucose oxidation. Figure 3 shows the CV of ZnO-GCE versus different glucose concentrations ranging from 2 to 10 mM. It is intriguing that the peak current decreased in a linear manner with glucose concentration. Other authors also observed similar behaviour for glucose oxidase immobilised on hexamine ruthenium (III) chloride \([\text{Ru(NH}_3]_6\text{Cl}_3]\) containing a nitrocellulose strip for urine glucose. They also demonstrated a linear decrease in peak current with increasing glucose density (Park et al., 2005). Possible reasons could be explained by mixing of analyte glucose sample in bulk electrolyte artificial sweat solution and its dependent electrochemical reaction at the ZnO-GCE electrode, which probably influenced the concentration variation in oxidation of produced \(\text{H}_2\text{O}_2\) and reduction of \(\text{O}_2\). In addition, air saturation in artificial sweat solution and the existence of interferents in the sweat samples may have decreased the peak electrocatalytic current.

Based on the obtained results, the next step would be to prepare a biosensor which is flexible, lightweight and durable. The sensing part would include a ZnO NPs-GCE working electrode able to detect glucose in sweat. Figure 4A shows schematically the preparation of such a prototype (whose photo is presented in Figure 4B), with the following steps:

- Preparation of a shadow mask to deposit contact electrodes Au/Ti or Ag via sputtering or thermal evaporation technique.
- Drop-cast of Ag/AgCl ink which will play the role of a reference electrode.
- Sputtering of Au metal which will serve as a counter electrode.
- Drop-cast of ZnO nanomaterial prepared by laser ablation which serves as the working electrode.

**Fig. 4.** Schematic presentation of preparation of biosensor device based on ZnO NPs-GCE (A) and a picture of prototype of same biosensor (B).

**Conclusions**

The present study demonstrated the successful employment of ZnO nanoparticles (NPs) produced by laser ablation in water for electrochemical oxidation of glucose. The NPs were then used for the preparation of ZnO NPs-GCE as a working electrode for electrochemical detection of glucose in artificial sweat solution. The CV measurements demonstrated changes in the current peak intensity with the concentration of glucose, confirming the possibility of using this sensor for the preparation of flexible wearable device. Steps in that direction were made by optimising a procedure and preparing a thin transparent flexible poly(dimethylsiloxane), PDMS, substrate, which will serve as support for the electrochemical biosensor. The flexibility of the PDMS sheet will provide excellent contact with the natural curves on the human skin texture, thus enabling good contact between the tested fluid, sweat, and the working electrode of the device.

This modern concept for "lab-on-chip" applied in space technologies is very suitable for the mining industry as well. The small size and light weight of the sensor under development will not interfere with the working process and its durability will permit remote monitoring in real time for a long period. Such flexible and wearable biosensors can provide great opportunity for companies to invest in the work environment and well-being of their employees, which will lead
to new and improved perception of the mining industry, increasing its attractiveness in terms of safety.

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SUSTAINABLE EXTRACTION AND PROCESSING OF RAW MATERIALS JOURNAL, 2022

REPROCESSING OF MAGNESITE BENEFICIATION-WASTE TO RECOVER MINERAL VALUE AND MINIMISE ENVIRONMENTAL FOOTPRINT

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ABSTRACT. The current paper deals with the re-processing of mineralised mine waste from magnesite processing operations aiming at the recovery of the value. Two cases of mineralised waste were examined. First, waste derived from the removal of "fine" before hand-sorting, with particle size of < 40 mm; this waste is usually stockpiled, comprises mostly of relatively coarse particles and is of relatively high-grade in magnesite. The separation methods applied were sorting, sink-float tests and magnetic separation. In general, the results from the application of physical separation methods were satisfactory. Commercial concentrates were obtained from sorting with MgCO3-grade ranging between 94 and 97% MgCO3 and yield about 46%, in case of mixing concentrate with middling, yield rises to 58-64% while grade slightly drops to 91-94%. Equally satisfactory were the results from sink-float separation at sp.gr. 2.86 (grade 95%, yield 45%) but questions arise from the small sp.gr. difference of magnesite and gangues. Finally, the less satisfactory results obtained from magnetic separation (grade around 80-85%, yield 33-65%) may be due to inefficient particles liberation and higher magnetic field is maybe required. Second, mineralised waste consisting of fine particles from size reduction operations were tested. These fines were processed with selective magnetic coating as well as co-agglomeration / magnetic separation techniques. In general, the results of physico-chemical processing of fines were very encouraging both on single minerals and their artificial mixtures. In case of magnetic coating, the effect of pH, collector concentration and kerosene dose was studied first on single minerals. Optimum results were obtained for pH=9, dodecylamine soaps 4.5x10-4 M and kerosene 2.5 L/t. Tests on artificial mineral mixtures at optimum conditions and magnetic separation at 0.8 A resulted in non-magnetic product with MgCO3-grade higher than 99%. The parameters examined in co-agglomeration / magnetic separation tests were the same as with magnetic coating. Best conditions for co-agglomeration on single minerals were pH=6, dodecylamine 2 kg/t, kerosene 4 L/t. Tests on mineral mixture reveals that the MgCO3-grade increases with dodecylamine but the yield drops.

Key words: magnesite, serpentinite, waste, hydrophobic agglomeration.

Introduction

As human progress and economic prosperity strongly depend on mineral commodities, the need for continuously increasing demand of mineral raw materials results in equally increasing amounts of mineral commodities extraction and processing with subsequent generation of considerable amounts of waste rocks and tailings. Each year, billion tonnes of wastes and tailings are generated from various mining and processing activities, collectively called “extractive waste”. The amount of waste is different for each mineral commodity, ranging from some kilograms per kilogram of product for high-grade commodities (e.g. coal, bauxite, iron ores) to several million tonnes per tonne of product for low-grade or complex ores such as gold ores (EC-JRC, 2009; IAI, 2015). Only in EU, the amount of the total extractive waste generated in the period 2004-2014 roughly ranges between 550 and 750 Mt/year (Eurostat, 2015) while the estimation for the global extractive waste is over 100 billion tonnes per year (Rankin, 2015).

If not managed properly, the large volumes of extractive waste can have severe impacts on environment; consequently, proper management strategies are required both in short- and long-term (Adiansyah et al., 2015). Depending on their particle size and prior processing, these wastes are deposited in purpose-specific areas, known as Extractive Waste Facilities (EWF), either in the form of waste rock heaps or tailing dams. The listed EWFs in the EU-28 that are in operation, in the process of being closed, or abandoned amounted to about 9700 units (Garbarino et al., 2018). The increasing demand for mineral values leads to the extraction and processing of even lower-grade orebodies, the generation of greater quantities of very fine particles deposited as tailings and the corresponding loss of mineral values, since separation methods are not very efficient for fines (Anastassakis, 2012). From the aforementioned, it derives that wastes are categorised into “mine waste”, which has no economic value and is rejected, and “mineralised mine waste”, which contains some quantity of mineral value and presents future potential economic prospects (Lottermoser, 2010). Consequently, the mineralised waste material could be considered a potential deposit for future mining and, after reprocessing, for value recovery (Anastassakis, 2002). This way of mining has several advantages over the traditional one, as less energy is required for extraction, transportation, reprocessing and recycling. In this way, extractive activities meet the fundamental principle of “recovery and recycling” and become more sustainable. The prerequisite for this consideration is the application of efficient reprocessing methods, the high-grade product and the positive overall economic outcome.

From the aforementioned, it is clear that extraction and mineral processing are unsustainable processes, since they create pollution and fail to entirely recover values, due to their fine particle size or their imperfect liberation from gangue. The current paper deals with the recovery of magnesite as a) coarse, rejected onto heaps and b) very fine particles, usually deposited into dams. Magnesite is the most important mineral of magnesium. Especially for Greece, it constitutes one of the most important primary raw materials, being exploited and exported since many years ago as concentrate, caustic or caustic calcined magnesia (produced by magnesite heating to 620-680°C), and dead-burnt magnesia (produced by heating to a temperature
higher than 1450°C, usually at 1800°C or even more, and for longer time) (Dimopoulos, 2012).

Magnesite itself is mainly used in the production of fertilisers, but also electrodes and tiles as well. Caustic magnesia is used in the production of panels, industrial floors and abrasives, in pyro-metallurgy as desulphurising agent and flux, as well as in hydro-metallurgy, environmental protection, fuels additive, pharmaceuticals, etc., with the use being dependent on MgO grade. Dead-burnt magnesia is mainly used in the production of refractory mass for metallurgical applications, cement and chemical industry. The higher MgO content is, the better is the quality of dead-burnt magnesia and its refractory properties. The samples originate from Evia Island, on which the exploitation of magnesite initiated in 1893.

A sorting stage was included as part of the entire flowsheet of the plant with prior discard of the ‘fine’ ore particles (-40 mm) in heaps, not amenable to efficient sorting according to the industrial schedule but being mineralised waste. Till recently, the stockpiled mineralised waste was amounted to about 250000 tonnes, with a relatively high grade in magnesite mineral (about 50%).

The target of the current work is to investigate the possibility to produce a commercial magnesite concentrate from a) hand-sorting “fine” tailings using physical separation methods and b) from very fine particles lost in tailings not efficiently separated from gangue using selective agglomeration methods (magnetic coating, co-agglomeration).

**Method and Materials**

**Case 1**

The material used in the current work was the aforementioned -40 mm fraction that was removed as fine before industrial hand-sorting. Two representative samples were obtained; one with particle size -40+10 mm and another with -10+2.36 mm. The later sample was sieved into fractions as follows: -10+4.75 mm whose weight was 22% w/w of the total, -4.75+2.36 mm with 27% w/w and -2.36 mm with 51% w/w; each one submitted to the corresponding separation. The liberation degree of the initial samples ranged from 81% for the -40+10 mm fraction to 93% for the -2.36 mm.

The tests on single minerals were carried out in a beaker of 400 mL. A total of 2 g-sample of magnesite or tailing was conditioned in 300 mL dodecylamine (DDA) solution of certain concentration. The pH of the suspension was regulated at the desired value and the suspension was conditioned for 3 min. Subsequently, only the gangue was submitted to wet high-intensity magnetic (WHIM) separation; the products of magnetic separation were collected, dried and weighted. In reference to the artificial mixture, the procedure was the same except the weight of the material that was 5 g of solid suspended in 750 mL of DDA solution. After conditioning, the mixture was fed to WHIM separator using a peristaltic pump. In this case, the MgCO$_3$ content of the products was determined by Thermal Gravimetric Analysis (TGA).

The reagents used in Case 2 were: DDA, NaOH and HCl solutions for pH adjustment, kerosene, and emulsifier when necessary. Both single minerals and artificial mixtures were used. The ratio of magnetite / serpentine was 50/50 in magnetic coating and magnetite / total gangue 75/25 in co-agglomeration.

**Results and Discussion**

**Case 1**

The -40 mm industrial waste was tested into hand-sorting, sink-float and magnetic separation. The results are presented below (Dimopoulos, 2012; Dimopoulos and Anastassakis, 2013).

**Results of sorting**

The metallurgical results of sorting are presented in Table 1. For process analysis reasons, three products (concentrate, middling, tailing) were obtained instead of two (concentrate, tailing), which is the usual case in electronic sorting. The products were analysed through TG analysis. As regards the size fraction -40+10 mm (Table 1), a clearly marketable concentrate may be produced by sorting. In case of mixing middling with concentrate, the concomitant product is of slightly lower grade but it still remains marketable (higher than 90%) with MgCO$_3$ recovery approaching 91.5%.
For particle size -10+4.75 mm, the grade of the concentrate increases to 97% MgCO₃, while the grade is slightly reduced to the equally marketable value of 93.6% MgCO₃ after mixing with middlings. The corresponding MgCO₃ recovery for the pure concentrate is 68.1% and increases to 92% by mixing middling with concentrate. Finally, the tailing may be rejected as it is, because of its low grade in MgCO₃. In case of merging concentrate and middling, the MgCO₃ losses to the tailing are only 8%. The successful separation is clearly denoted by the different colour of the products after microscopy examination (Figure 1).

### Table 1. Results of sorting

<table>
<thead>
<tr>
<th>Particle size mm</th>
<th>Product</th>
<th>Weight %</th>
<th>MgCO₃ %</th>
<th>MgCO₃ distribution %</th>
</tr>
</thead>
<tbody>
<tr>
<td>-40+10</td>
<td>C</td>
<td>47.2</td>
<td>93.7</td>
<td>75.9</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>11.3</td>
<td>80.0</td>
<td>15.5</td>
</tr>
<tr>
<td></td>
<td>C+M</td>
<td>58.5</td>
<td>91.1</td>
<td>91.4</td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>41.5</td>
<td>12.0</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>100.0</td>
<td>58.2</td>
<td>100.0</td>
</tr>
<tr>
<td>-10+4.75</td>
<td>C</td>
<td>46.2</td>
<td>97.0</td>
<td>68.1</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>18.4</td>
<td>85.2</td>
<td>23.9</td>
</tr>
<tr>
<td></td>
<td>C+M</td>
<td>64.6</td>
<td>93.6</td>
<td>92.0</td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>35.4</td>
<td>15.0</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>100.0</td>
<td>65.8</td>
<td>100.0</td>
</tr>
</tbody>
</table>

* C: Concentrate, M: Middling, T: Tailing, F: Feed

### Table 2. Results of sink-float separation at sp.gr. 2.88

<table>
<thead>
<tr>
<th>Product</th>
<th>Weight %</th>
<th>MgCO₃ %</th>
<th>MgCO₃ distribution %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sink</td>
<td>45.07</td>
<td>95.0</td>
<td>72.2</td>
</tr>
<tr>
<td>Float</td>
<td>54.93</td>
<td>30.0</td>
<td>27.8</td>
</tr>
<tr>
<td>Feed</td>
<td>100.00</td>
<td>59.28</td>
<td>100.00</td>
</tr>
</tbody>
</table>

The results clearly show that magnesite separation from tailings is feasible at this sp. gr., since a commercial grade concentrate of 45% yield and 95% MgCO₃ is obtained. On the other hand, the small difference in sp. gr. between magnesite and gangue minerals (magnesite 2.98, dolomite 2.84, serpentine 2.60) denotes that there might be difficulties with respect to their separation by gravity methods. This is sustained by the relatively high grade of the tailings in magnesite and the losses of magnesite in the tailings.

### Results of magnetic separation

The equipment used for magnetic separation was a drum separator with permanent magnet. The results of magnetic separation are presented in Table 3.

### Table 3. Results of magnetic separation

<table>
<thead>
<tr>
<th>Particle size mm</th>
<th>Product</th>
<th>Weight %</th>
<th>MgCO₃ %</th>
<th>MgCO₃ distr. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>-10+4.75</td>
<td>NM*</td>
<td>64.9</td>
<td>84.8</td>
<td>92.4</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>35.1</td>
<td>12.8</td>
<td>7.6</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>100.0</td>
<td>59.5</td>
<td>100.0</td>
</tr>
<tr>
<td>-4.75+2.36</td>
<td>NM</td>
<td>62.8</td>
<td>80.5</td>
<td>89.9</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>37.2</td>
<td>15.3</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>100.0</td>
<td>56.2</td>
<td>100.0</td>
</tr>
<tr>
<td>-2.36</td>
<td>NM</td>
<td>33.5</td>
<td>86.8</td>
<td>59.2</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>66.5</td>
<td>30.0</td>
<td>40.8</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>100.0</td>
<td>49.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

*NM: Non-magnetic, M: Magnetic, F: Feed

From this Table, it is clear that the results are generally inferior in comparison to hand-sorting and sink-float tests. More specifically, a non-magnetic concentrate of marginally commercial grade can be produced only for particles -2.36 mm. In addition to its relatively low quality, this product has also a very low yield and MgCO₃ recovery. The grade of the fraction -10+4.75 mm is slightly less than the commercial but its recovery in MgCO₃ is high. In regard to the particles -4.75+2.36 mm, the grade of the concentrate is the lowest among the three size fractions but the recovery in MgCO₃ is high enough. The comparison of magnetic separation to the other methods reveals that, in general, the yield of the concentrate is higher but the grade is lower, which could be attributed to the existence of non-magnetic minerals (e.g., dolomite, talc) in the magnesite concentrate.

### XRD analysis

XRD analysis of the magnetics for particles -2.36 mm detected magnesite, sepiolite, serpentine, talc (possibly non-liberated from magnetic minerals), and amphibole.

### Case 2

This case refers to the separation of fine magnesite particles from similar size gangue. The generation of fine
particles is inevitable in many processing operations of mineral commodities. Especially in cases of low-grade ores, the value mineral has to be ground to very fine size to achieve high liberation degree, because of its finely disseminated form and mineralogical texture. The separation of fine mineral particles presents considerable difficulties, because of the peculiar properties of fine particles (Fuerstenau et al., 1979). Due to these properties, a lot of effort has been devoted to their separation through physicochemical methods which are primarily based on the modification or combination of standard separation methods, such as flotation (Rulyov, 2016; Hoang et al., 2021; Sajjad and Otsuki, 2022), agglomeration or combination of agglomeration with flotation (Anastassakis, 2012; Yang et al., 2016). In the current work the results of magnetic coating and agglomeration / magnetic separation are employed.

**Results of magnetic coating - discussion**

Figure 2 shows the magnetic separation of single minerals (magnesite, serpentine) after their conditioning with magnetite in the presence of DDA.

As it derives, the recovery of fine serpentine particles to the magnetic product is almost complete throughout the entire pH range between 6 and 11, which denotes that serpentine particles obtained a magnetic coating by controlling the surface properties of serpentine and magnetite fine particles. Microscopic examination of serpentine particles after coating reveals that they obtained a strong magnetic coating (Figure 3). The magnetic coating occurred not only on single particles but also on agglomerates of serpentine particles.

The results of Figure 2 denote that magnesite practically obtains no magnetic coating till pH=9. This is confirmed by Figure 3b, which shows the results for pH=6. For pH>9, the coating of the surface of magnesite particles increased with pH but, even in the very basic pH region, the percentage of the magnetically-rendered magnesite was less than 20%.

Microscopic examination of magnesite particles after coating revealed that, in any case, the magnetic coat was much less extended and less strongly attached than in the case of serpentine.

**Results of agglomeration / magnetic separation - discussion**

In these tests, the effect of pH and DDA dose was examined. Conditioning time was kept constant at 3 min, settling time at 30 sec and agitation speed at 210 rpm. The effect of pH was studied with DDA dose of 1 kg/t while that of DDA dose at pH=8.

The dependence of hydrophobic agglomeration with pH is shown in Figure 5. As observed, the weight of the settled co-agglomerated gangue (mixture of serpentine, ilmenite, olivine) is much higher than that of magnesite throughout the entire pH range 7 to 11, remaining practically constant (around 78%). For magnesite, no agglomeration practically occurs in the slight alkaline region (pH=7-9) while the weight of the settled mineral
increases for pH=10-11, but it remains much lower than that of gangue (max 8.5% at pH=11).

Consequently, selective hydrophobic agglomeration of gangue with the use of DDA seems feasible for pH = 7-9.

Microscopic observation of the settled products at pH=8 reveals that magnesite is encountered either as single particles or small clusters of weakly-held agglomerates (Figure 6a), while the fine particles of the gangue mineral mixture have formed relatively large and strong agglomerates (Figure 6b).

Magnetic separation tests on the agglomerated gangue mixture revealed that a relatively high percentage (between 75-85%) was allocated to the magnetics. This is due to the co-agglomeration of all the three gangue minerals, out of which at least ilmenite possesses strong magnetic properties while serpentine and olivine possess weak to non-magnetic properties. Consequently, these clusters are attracted by the magnetic field. Microscopic examination of the products revealed that the magnetic product was mostly composed of relatively large-size gangue co-agglomerates while the non-magnetic gangue was composed of much smaller size, loosely held agglomerates or even single gangue particles.

The effect of DDA dose on the agglomeration of single minerals was investigated next, for DDA additions of up to 2.0 kg per tonne of mineral (Figure 7). The results clearly show that magnesite is slightly affected for DDA additions lower than 2 kg/t; on the contrary, the weight of the agglomerated gangue...
continuously increases with DDA dose, reaching to approximately 86% for DDA 2.0 kg/t of mineral.

Microscopic observations, not presented here, reveal that the settled gangue (serpentine, ilmenite, and olivine mixture) is comprised of co-agglomerated fine particles in all cases. Also, the increase of DDA addition results in stronger and larger size agglomerates. On the contrary, magnesite fine particles are mostly encountered as single particles or loose agglomerates. The addition of kerosene along with DDA 2 kg/t, at pH=8, had a comparatively stronger impact on magnesite than on gangue, as the weight of the settled product increased significantly to about 15% (compared to about 8.5% without kerosene). The weight of the settled gangue increased to 94% (compared to 85.9% without kerosene) but the addition of kerosene resulted in tighter gangue agglomerates than using DDA only.

After experimentation on single minerals, tests were carried out on magnesite / gangue artificial mixtures of 3 / 1 ratio and DDA / kerosene mixtures of 2 / 1 ratio with varying DDA dose (Figure 8). As shown, the increase of DDA dose is beneficial to magnesite concentrate (non-magnetic), as its grade increases gradually from 75% (feed) to approximately 95%, which means improvement of the feed grade by 25%. In reference to recovery, there is a gradual drop with amine addition but it still remains satisfactory.

Conclusions

As mineral deposits extraction has shifted to even lower grades and mine waste volumes are even larger, the recovery of the initially discarded value mineral, under favourable technical and economic circumstances, will render mining more sustainable by saving resources from rapid depletion, securing resources for future generations, reducing energy consumption for extraction, saving water for ore processing and reducing areas for waste disposal.

This work deals with the recovery of magnesite from waste, deposited in waste heaps, by applying traditional physical separation methods for the coarse and physicochemical (magnetic coating and co-agglomeration/magnetic) separation techniques for the fines.

The results in both cases proved satisfactory and may be applied in other cases as well. In more details:

- Among the physical methods tested (sorting, sink-float tests and magnetic separation), the most efficient proved sorting. Commercial concentrates were obtained from sorting of high MgCO$_3$-grade (between 94 and 97% MgCO$_3$) and yield about 46%. The yield can be improved to 58-64% by merging the concentrate with middling but the grade slightly drops (to 91-94%).

- Regarding sink-float separation, the results are equally satisfactory at sp.gr. 2.08, as the grade of the sink product was high enough (95% MgCO$_3$) and the yield 45%; however, the separation by gravity method seems very difficult, if not impossible, because of the small difference in sp.gr. between magnesite and gangues.

- Finally, less satisfactory results are obtained from magnetic separation (grade around 80-85%, yield 33-65%), which could be attributed to the inefficient particles liberation. The application of stronger magnetic field could improve the results. In general, the results from the application of physical separation methods are considered satisfactory.

- As great portion of mineralised waste derives from operations of size reduction to fine particle size and the problem is expected to be more intense with the extraction of even lower grade ores, the second series of tests was carried out on fine particles by applying physicochemical methods. These fines were processed with selective magnetic coating as well as co-agglomeration / magnetic separation techniques. Tests were carried out both on single minerals and their mixture. In case of magnetic coating, the effect of pH, collector concentration and kerosene dose was studied first on single minerals. Optimum results were obtained for pH = 9, dodecylamine solution 4.5x10$^{-5}$ M and kerosene 2.5 L/t. Tests on artificial mineral mixtures at optimum conditions and magnetic separation at 0.8 A resulted in non-magnetic product with MgCO$_3$-grade higher than 99%. The parameters examined in co-agglomeration / magnetic separation tests were the same as with magnetic coating. Best conditions for co-agglomeration on single minerals were pH=8, dodecylamine 2 kg/t, kerosene 4 L/t. Tests on mineral mixture reveal that the MgCO$_3$-grade increases with dodecylamine but the yield drops. In general, the results of physicochemical processing of fines were very encouraging both on single minerals and their artificial mixtures. Considering the complex physicochemical
behaviour of magnesite, the results are also very promising for further application to other mineral systems.

In summary, the reprocessing and recovery of value from mineralised waste, where possible, should enhance the overall extraction economics and reduce the environmental impacts from mineralised waste rejection, making mineral extraction and processing operations more sustainable.

References


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ON USING EXCESS GIBBS ENERGY AS AN INDICATOR OF HYDROPHOBICITY IN THE FLOTATION PROCESS

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ABSTRACT. It has been shown that the partial molar excess Gibbs energy ($G^\text{ex}$) can be used as an indicator of hydrophobicity and hence contributes to explaining the behaviour of collectors in the recovery of minerals by flotation. This is because hydrophobicity of a mineral particle on which a collector is adsorbed is related to the fact that the alkyl chain associated with the collector behaves in the same way as any hydrocarbon would in a non-ideal mixture with water. Such mixtures are quantified thermodynamically by determining the activity coefficient of the hydrocarbon moiety of the collector and hence its $G^\text{ex}$ in the mixture. The present paper is aimed at extending the above concepts in two different ways. Firstly, an investigation is made of the relationship between $G^\text{ex}$ and contact angle and/or recovery for systems such as ionic liquids and aminothiophenols. Secondly, on the basis of the observation that increases in $G^\text{ex}$ are indicative of increases in the hydrophobicity of the mineral particle-collector aggregate, a study was undertaken to examine, respectively, the effects of the presence of electrolytes or alcohols in the system, of pH and changing concentrations of the collector, on $G^\text{ex}$ of the collector alkyl group and hence its hydrophobicity. In the first instance, the relationship between $G^\text{ex}$ and contact angle and recovery is sustained. With respect to the latter, the absence of any correlation between $G^\text{ex}$ and recoveries supported the proposition that the major effect of electrolytes and added alcohols is rather on particle – bubble attachment. Similarly, it is also indicated that since the change in $G^\text{ex}$ is minimal when collector concentration or pulp temperature is increased these changes do not significantly affect the hydrophobicity of the collector-mineral particle and hence also the recovery in a microflotation.

Key words: hydrophobicity, partial molar excess Gibbs energy, reagents, flotation.

Introduction

As is well known the main purpose of using a collector in the flotation of ores is to render the mineral particles which are to be recovered hydrophobically. Classical contact angle has been used to indicate hydrophobicity and there is voluminous literature on the measurement of contact angles as well as the relationship between contact angle and recovery (e.g., Fuerstenau et al., 1957; Bogdanov, 1957). However, it has been pointed out (Nagaraj and Ravishanker, 2007) that although contact angles in single mineral systems have been correlated with mineral flotation, they are poor predictors of flotation performance in real systems with complex mineralogy. There have also been attempts to use the concept of the hydrophilic-lipophilic balance (HLB) number to characterise the hydrophobicity imparted by reagents (e.g., Laskowski, 2003; Pugh, 2007; Zhang et al., 2012). The HLB number represents an empirical numerical correlation of the emulsifying and solubilising properties of different surface-active agents (Davies, 1957). However, in its original context the HLB number was an early attempt to show how the molecular structure is related to hydrophobicity. Modern thermodynamics is now far advanced in this regard through the determination of the activity coefficient or $G^\text{ex}$ as the more appropriate way in which to define the behaviour of molecules in a non-ideal solution. In that regard the hydrocarbon associated with the collector adsorbed onto the mineral particle in a pulp and its water environment represents a classical non-ideal solution. Corin and O’Connor (2014) showed that using the concept of excess Gibbs free energy it was possible to predict the behaviour of frothers/surfactants in multi-component mixtures of different concentrations and is thus arguably a more robust method of characterising the hydrophilic-lipophilic behaviour of frothers than the HLB number. The excess Gibbs energy related well to the HLB number but has the added advantage of showing the effects of different concentrations of the surfactant in water and other multi-component systems as well as, if necessary, temperature effects. Harris and O’Connor (2017) have shown how that there is generally a strong linear relationship between the excess Gibbs energy of collectors with different alkyl chain lengths and frothers with different alkyl chain lengths and bubble size, surface tension or froth behaviour. This is indicative of the key role which the non-polar group of these reagents plays in determining the changes which occur when using reagents of different alkyl chain lengths. Since the theory of the role of the alkyl chain is related to the formation of hemi-micelles those results are also proposed to provide quantitative thermodynamic confirmation of the role of hemi-micelles in the determination of the indicated flotation parameters. In a further extension of these investigations, O’Connor (2021), based on the assumption that flotation recovery in a microflotation cell is a good indicator of the hydrophobicity of a mineral particle since it simply measures the extent to which a particle is able to attach to a bubble sufficiently strongly to be able to report to the launder, showed that the behaviour of collectors with different alkyl chain lengths had a strong positive linear relationship between partial molar excess Gibbs energy of the alkyl moiety of the collector and the flotation recovery and the contact angle thus confirming that the partial molar excess Gibbs energy of the alkyl chain is indicative of the force driving the mineral particle to remove itself from the aqueous (water) to the gas (bubble) phase.

The present paper further interrogates the hypothesis that it is the non-ideality of the hydrocarbon-water system, as indicated by the $G^\text{ex}$ of the hydrocarbon moiety of the collector, which provides the driving force to transfer the mineral-collector particle aggregate from the water to the bubble and that the greater the value of the $G^\text{ex}$ the greater is that driving force. Given that the hydrophobicity of the particle, especially in a microflotation cell, is reflected in its recovery there should be a robust relationship between $G^\text{ex}$ and recovery. In
particular, ionic liquids and aminothiophenols were investigated. This paper has also investigated the extent to
which factors such as pH, presence of other species such as electrolytes or alcohols in the water, changes in concentration
and pulp temperature, affect the $G^\text{ex}$ and hence whether these changes can be used to interpret previously reported results,
where available, on the influence these factors have on flotation recoveries.

Methods to estimate activity coefficients and partial molar excess Gibbs energy

As indicated above the hydrocarbon associated with a collector molecule adsorbed onto a mineral particle when
located in an aqueous environment represents a classical thermodynamically non-ideal solution. Such non-ideal solutions
are quantified by determining the activity coefficient, and subsequently the $G^\text{ex}$ of the hydrocarbon at a given molar
concentration. The collector molecule is adsorbed onto the mineral particle via a chelating ligand such as typically
represented by a thiol end group in the case of xanthates or an NH$_2$/HS group in the case of aminothiophenols. The
hydrocarbon is associated with the collector in these instances via an oxygen atom and thus using the alcohol of the relevant
alkyl group is an appropriate proxy for the behaviour of the hydrocarbon group of the collector.

There are many methods described in the literature to estimate activity coefficients. Of the more modern methods the
UNIFAC (Uniquac Functional-group Activity Coefficient) method (e.g., Fredenslund et al., 1977; Sandler, 2006) has
been widely used. More recently the COSMO-SAC model (Xiong et al., 2014) has been used. There are numerous
papers in the literature comparing these approaches and some suggest that COSMO-SAC may be slightly superior for
aqueous systems (e.g., Gerber and Soares, 2010). In any event the activity coefficient is an indicator of the combined
effects of properties such as total molecular surface area, molecular volume, molar volume and molecular weight of the
constituent functional groups for each of the compounds. In determining activity coefficients using COSMO-SAC the
temperature was set at 298.15 K, total pressure at 101.325 kPa and, unless otherwise stated, the mole fraction of the
collector at 0.0001 which equates fairly well to typical concentrations used in industrial flotation plants. The activity
coefficient in turn is used to determine the $G^\text{ex}$, the excess value being the difference between the values for a real as
opposed to an ideal mixture. The most useful excess thermodynamic property is the $G^\text{ex}$ since this term incorporates
the enthalpic and entropic contributions. The $G^\text{ex}$ is calculated using its relationship to the activity coefficient, $\gamma$, viz

$$G^\text{ex} = RT \ln \gamma$$

where $R$ is the universal gas constant and $T$ is the absolute temperature. It is important to note that the $G^\text{ex}$ is not the same
as the surface free energy (e.g., van Oss and Good, 1988) or the free energy of collector adsorption as expressed by, for
example, the Stern-Grahame equation (e.g., Fuerstenau et al., 1970). As mentioned in the introduction the various
experimental values of recovery and/or contact angles used in this investigation were obtained from the published literature.
The source of the data is indicated in the references in the relevant sections. Unless otherwise stated the flotation
recovery data were obtained in microflotation cells.

Results and discussion

Further evidence that partial molar excess Gibbs energy ($G^\text{ex}$) is indicative of hydrophobicity as indicated by flotation recovery in the case of ionic liquids and aminothiophenols

As previously reported (O’Connor, 2021) flotation recovery in a microflotation cell is an excellent indicator of the extent to
which a mineral particle has been rendered hydrophobic since it allows for all the variables resulting from a complex
mineralogy of the particle and simply indicates the propensity of the collector-particle aggregate to attach to a bubble and
ultimately to report to the concentrate. Sahoo et al (2016) reported on the flotation of quartz using ionic liquids with
different functional groups and varying alkyl chain lengths. They concluded that the flotation results imply that the alkyl
chain length plays a major role in determining the floatability of the quartz compared to the interaction pattern of the ionic liquid
with the quartz. This can be confirmed by applying the concept of $G^\text{ex}$ to the flotation results. Table 1 shows the values of the $G^\text{ex}$ for the respective alkyl groups for each ionic liquid (as
determined for the alcohol of that alkyl group) and the recoveries of quartz (Figure 1). Clearly there is a good
relationship between recovery and $G^\text{ex}$ ($R^2=0.93$).

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Activity coeff.</th>
<th>$G^\text{ex}$ (kJ/mol)</th>
<th>Quartz recovery*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-methyl-3-octyl imidazolium chloride</td>
<td>123</td>
<td>11.92</td>
<td>20</td>
</tr>
<tr>
<td>1-n-decyl-3-methyl imidazolium tetrafluoroborate</td>
<td>273</td>
<td>13.89</td>
<td>68</td>
</tr>
<tr>
<td>1 n hexyl 3 methyl imidazolium chloride</td>
<td>47</td>
<td>9.54</td>
<td>12</td>
</tr>
<tr>
<td>cetyl pyridinium bromide</td>
<td>1393</td>
<td>17.93</td>
<td>100</td>
</tr>
</tbody>
</table>

*Est. from Figure 3

In a similar context it is of interest to use results reported by Marabini et al. (2007) studying the effect of changing structures of various collectors, on the recoveries of Zn (mainly smithsonite) and Pb (mainly cerrusite). In one set of studies the effect of changing the alkyl group on aminothiophenol reagents for which the core structure is shown in Figure 2 and the variations in the alkyl group, R, bonded to the oxygen atom. Reagents in which the alkyl group R ranged from methoxy (CH$_3$O) to hexyloxy (C$_6$H$_{13}$O) were used in the flotation tests.

The flotation tests were carried out in a standard laboratory batch flotation cell which, for the present purposes, is less ideal than using a microflotation cell. The results of Zn recoveries as a function of $G^\text{ex}$ are shown in Figure 3 which shows that there is a clear trend in the relationship between the recovery of Zn and the $G^\text{ex}$ of the various alkoxy chain lengths.
they had reported that the presence of nitrate and sulphate ions resulted in a significant increase in recovery in both galena and chalcopyrite. The microflotation tests were carried out in water with an ionic strength of 0.0241 mol/L and 0.241 mol/L respectively as well as in deionised water and using SIBX as the collector. In the case of galena the recoveries were 58% and 87% for the two increasing ionic strengths and for chalcopyrite were 84% and 88%, respectively. Not surprisingly, given how easily chalcopyrite floats even in the absence of a collector, the effect of the ionic strength was minimal. The effect of the presence of electrolytes on G\text{ex} was then investigated by using H₂SO₄ (sulphate ions) at constant mole fraction of 0.05 and of the alkyl group of 0.05. The calculations were carried out for a range of xanthates from ethyl to pentyl. The effect of the presence of sulphate ions on G\text{ex} of the alkyl group compared to the values in the absence of the acid is shown in Table 2.

As expected, the values of G\text{ex} in the absence of acid increased as the alkyl chain length increased as had been previously reported. However, it is clear that the presence of SO₄²⁻ ions in fact reduced the values of G\text{ex} indicating that the presence of ions had not increased the hydrophobicity of the mineral – collector aggregate as per the underlying hypothesis. Similar observations were made for the effect of the presence of nitrate ions (HNO₃). These results are therefore consistent with the proposition by those authors that the main effect of the presence of the electrolytes was on the extent of bubble-particle attachment.

**Effect of pH on partial molar excess Gibbs energy (G\text{ex})**

In a manner similar to the behaviour of the electrolytes the role that pH has on hydrophobicity and hence recovery can be investigated using G\text{ex}. In a study of the effect of pH on the contact angle and recovery in a quartz / dodecylamine (DDA) system it was shown that as pH increased from 2 to 10 the contact angle increased from about 20° to > 80° (Fuerstenau, 1957). In order to investigate whether this effect was also observed in the values of G\text{ex}, G\text{ex} values for DDA were determined at decreasing mole fractions of H₂SO₄ of 0.15, 0.1, 0.05 and 0.005 while maintaining a constant mole fraction of DDA at 0.05. These reduced acid concentrations equate to an increase in pH. At these acid concentrations the values of G\text{ex} are 9.69, 12.93, 13.56 and 15.07 kJ/mol respectively. The increase in the values of G\text{ex} as pH increased are consistent with increasing hydrophobicity (microflotation recovery) and contact angles reported in the reference above. Although this result does not explain fundamentally the effect of changing pH, viz. H⁺/OH⁻ ratio, on the behaviour of the alkyl group it

![Fig. 1. Quartz recovery (%) vs G\text{ex} (kJ/mol) for various ionic liquids used in flotation (R²=0.93) (Sahoo et al., 2016)](image1)

![Fig. 2. Basic structure of aminothiophenol ion (Marabini et al, 2007)](image2)

![Fig. 3. Relationship between Zn recoveries using C1 to C6 alkoxy aminothiophenols and the G\text{ex} of the respective alkoxy groups (R² = 0.88) (Marabini et al, 2007)](image3)

**Table 2. Effect of presence of H₂SO₄ on G\text{ex} of various alkyl groups represented by their respective alcohols**

<table>
<thead>
<tr>
<th>Alkyl group of xanthate</th>
<th>G\text{ex} (kJ/mol) in presence of H₂SO₄</th>
<th>G\text{ex} (kJ/mol) in absence of acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl</td>
<td>1.95</td>
<td>3.24</td>
</tr>
<tr>
<td>Propyl</td>
<td>3.77</td>
<td>5.13</td>
</tr>
<tr>
<td>1 butyl</td>
<td>5.33</td>
<td>6.74</td>
</tr>
<tr>
<td>2-butyl</td>
<td>6.52</td>
<td>7.84</td>
</tr>
<tr>
<td>isobutyl</td>
<td>6.78</td>
<td>8.01</td>
</tr>
<tr>
<td>1-pentyl</td>
<td>6.83</td>
<td>8.28</td>
</tr>
</tbody>
</table>

It must be emphasised that the chelating action of the backbone structure (Figure 2) of the aminophenol on the Zn mineral is a constant in all cases.

As shown above, as well as in studies previously referred to, it now appears to be reasonable to hypothesise that G\text{ex} is a good indicator of the hydrophobicity of a mineral-collector aggregate both in terms of recovery, especially in a microflotation cell, and of contact angle. On that basis it was decided to investigate whether the presence of electrolytes had any significant positive effect on G\text{ex}. If such an effect was observed, it could be deduced that changes in flotation recovery in the presence of such electrolytes could be due to their effect on the non-ideal behaviour of the alkyl group of the collector in the aqueous environment. To investigate this hypothesis, data generated by October et al. (2020) on the effect of the presence of electrolytes on flotation recoveries as well as on bubble-particle attachment was used. In this study
does infer that, in terms of the underlying hypothesis, changes in pH do seem to have a direct impact on the hydrophobicity of the mineral-collector aggregate.

**Effect of alcohol species on partial molar excess Gibbs energy (G̅ex)**

It has been previously shown that many of the functions of a frother such as their effect on froth height, surface tension and critical coalescence concentration respectively are strongly related to the G̅ex of the alkyl groups associated with the reagent. It was demonstrated that it was possible to reasonably predict the performance of frothers based on the value of their G̅ex (Harris and O’Connor, 2017). Frothers are usually alcohols and there are numerous reports on the role which the addition of frothers may have on flotation behaviour. Hence, it is of interest to investigate whether the presence of an alcohol may influence the G̅ex of the collector being used given that the hypothesis proposed in the present paper is that the absence of such an effect would point to the role of the alcohol being other than influencing the hydrophobicity of the collector-particle aggregate. In the present instance data generated by Pienaar et al. (2019) on the effect of adding hexanol to SEX on the recovery of galena in a batch flotation cell showed that the effect of adding hexanol was to increase the first order flotation rate constant from 0.091 min⁻¹ to 0.190 min⁻¹ with the recovery after 6 min increasing from ~40% to 69%. This addition of hexanol, not surprisingly, resulted in a decrease in G̅ex of the ethyl group from 3.23 kJ/mol to 1.23 kJ/mol since hexanol as the 3rd phase in this non-ideal solution is more amenable to the presence of the alkyl group associated with the SEX. It can therefore be deduced that this reduction in G̅ex on the addition of hexanol suggests that the hydrophobicity is, if anything, reduced and that hence the increase in recovery when hexanol was present is arguably related to its effect on particle-bubble attachment phenomena at the air-water interface as was indeed proposed by these authors.

**Effect of increases in concentration of the reagents on partial molar excess Gibbs energy (G̅ex)**

In the flotation of sulphide minerals xanthates of varying alkyl chain lengths are widely used. The underlying hypothesis of this paper is that the alkyl groups increase the hydrophobicity of the mineral (sulphide)-collector (xanthate) aggregate by increasing the non-ideality of the solution in which these aggregates occur. The dosage of these collectors is an area of much research since it is often proposed that it is not necessary to add more than a pseudo-monolayer of collector to impart adequate hydrophobicity onto the mineral particle to which the collector is attached. To explore this further the effect of concentration on G̅ex, viz. the hydrophobicity of the mineral-collector aggregate, was investigated. Table 3 shows how the partial molar excess Gibbs energy changed as the concentration of a range of alkyl groups increased. The groups investigated are ethyl, propyl, 1-butyl, 2-butyl, 2-methyl-1-propyl and 1-pentyl. In each case the alcohol of the particular alkyl group was used.

These results highlight a number of issues related to the use of reagents with these alkyl group moieties. In fact they are typical of the range of xanthates which are widely used in industry such as sodium ethyl xanthate (SEX) or sodium iso-butyl xanthate (SIBX), i.e. 2-methyl-1-propyl xanthate. From this table it can be deduced that the alkyl group with the strongest ability to render the mineral particle hydrophobic is the isobutyl or 2-methyl-1-propyl group. This is consistent with the fact that SIBX is so widely used in industry. On the other hand, the ethyl group (e.g. SEX) is the weakest in that regard even though it is also widely used in industry. However, it is also interesting to observe that if increasing G̅ex values are indicative of increasing hydrophobicity, which has been amply demonstrated to be the case in the present and previous publications, then increasing the concentration of the reagent in the flotation process is fundamentally not necessarily conducive to increasing the hydrophobicity of the mineral-particle aggregate. This observation is also consistent with the widely held view that in many concentrators the operators may be overdosing with collectors. There are obviously many other factors to consider when selecting a collector since flotation is a highly complex process involving many interactions between collectors and, for example, frothers, activators, etc.

**Effect of increases in temperature of the pulp on partial molar excess Gibbs energy (G̅ex)**

It was mentioned in the Introduction that another advantage of using G̅ex instead of, for example, HLB as an indicator of hydrophobicity, is that it can also predict the effect of pulp temperature. Table 4 shows the effect of an increase in temperature from 298.15K to 308K for the range of alkyl groups covered in Table 3.

In each case an increase in temperature results in a very slight increase in the value of G̅ex except for, interestingly, a slight decrease in the value for the ethyl group. However, clearly in terms of the underlying hypothesis changes in temperature do not appear to significantly affect the hydrophobicity of the mineral-collector aggregate. It is much more likely that such changes will affect the rheology of the pulp which could have a significant effect on the flotation performance.

**Conclusions**

Previous publications by the authors and colleagues have indicated that a mineral particle, on which a collector containing a hydrocarbon moiety is adsorbed, when present in an aqueous system such as a flotation pulp, represents thermodynamically a classical non-ideal mixture.
Such systems are characterised by activity coefficients and hence $G^\text{ex}$. This has led to the hypothesis that there could be a relationship between the $G^\text{ex}$ of the hydrocarbon moiety associated with the adsorbed collector and its hydrophobicity as indicated by, for example, recovery in a micro flotation cell or contact angle. The present paper provides further evidence that continues to sustain this hypothesis when considering collectors such as ionic liquids or amino thiophenols in a quartz or sphalerite system respectively. It is shown that the effect of pH on hydrophobicity as indicated by $G^\text{ex}$ is consistent with previously reported contact angle and recovery results in a quartz / DDA system. In a further development of this hypothesis, it has been shown that when factors such as the presence of electrolytes or alcohols in the flotation pulp are investigated there was no indication that there was any increase in the hydrophobicity of the mineral-collector aggregate as indicated by $G^\text{ex}$ and recovery and that hence it may be reasonably deduced that the changes observed in flotation recovery in such cases are related to other phenomena such as particularly bubble-particle attachment. Similarly, it is also indicated that since the change in $G^\text{ex}$ is minimal when collector concentration or pulp temperature is increased these changes do not significantly affect the hydrophobicity of the collector-mineral particle and hence the recovery in a micro flotation recovery. Clearly, in a large turbulent tank cell, for example, there are many other factors which affect recovery but the entire recovery process is initially dependent on the attachment of the mineral particle to the bubble which is driven by the hydrophobicity of the mineral-particle aggregate which in turn appears to be a strong function of the partial molar excess Gibbs energy of the alkyl group associated with the collector.

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INDUSTRIAL SYMBIOSIS IN RAW-MATERIAL SECTOR AS AN OVERARCHING SOLUTION IN CIRCULAR ECONOMY

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ABSTRACT. Circular economy is a key instrument for reducing climate change and transition to green economy. The industrial symbiosis is a circular business model – a concept, discussed as a platform for exchange of materials among business companies in order to achieve sustainability and reduce waste. “Shared use” of wastes as raw-materials results in multiple benefits – economic (reduction of cost to produce raw materials), environmental (reduction of generated waste, reduction of CO2 emissions, opportunities for applying the green policies), as well as social benefits (creating “green” job positions, support to local communities). A discussion is presented in the paper on industrial symbiosis as an important opportunity for developing a circular economy by the established business model. A survey among thirteen (13) companies from the mineral raw-material sector has been performed and it has proved that companies are aware of the concept, even more – to a certain extent, companies perform the concept in their day-to-day activities. The paper has marked the need of actually mapped networks, which will model a sustainable industrial symbiosis.

Key words: industrial symbiosis, circular economy, mineral raw-material industry

Introduction

Rational use of natural resources is among the most important environment-related considerations, which underlies the bases of the initial European contracts. The roadmap to a resource efficient Europe (COM(2011)0571) is among the key initiatives of the Seventh Environment Action Programme. Deployment of the economic potential of the European Union in order to provide more productive economy concurrently with the use of less resource and converting from linear to circular economy is among the major objectives of the Programme. Adopted in 2018, the Circular Economy Package comprises measures that will assist the stimulation of transition of the European Union to circular economy by increasing the share of recycling and re-use by promoting competitiveness in worldwide plan, enhancing sustainable economic growth and creating new job positions.

Competitive measures for promoting re-use and stimulating the industrial symbiosis – converting the by-product of one sector into a raw material for another are among the elements, comprised by the Circular Economy Package of 2018.

The present report is a discussion on industrial symbiosis as one of the business models in circular economy, a business model that might result in implementation of its principles.

Nature of the concept of industrial symbiosis

Industrial symbiosis has been familiar since the 70-ties of the past century. The concept has been defined as a synergic exchange of refuse flows, by-products, water and energy among individual organisations in a certain area or region.

In its nature, the industrial symbiosis is a sub-sector of industrial ecology, which includes individual industries in a collective approach to competitive advantages, including physical exchange of materials, energy and services (Chertow, 2000). In particular, industrial process wastes may either be used by the processes of the same or another company as a substitute of industrial resources (i.e. water, raw materials, energy) or may be used in the production of new products to be sold on the market (Albino and Fraccascia, 2015).

The industrial symbiosis is characterised as a systematic approach toward a more sustainable and more integrated industrial system (Chertow and Ehrenfeld, 2012), which identifies business opportunities effecting on the insufficiently used resources (as raw materials, energy, water, opportunities, experience, assets etc.) (Lombardi and Laybourn, 2012). It includes organisations, operating in various sectors, which take part in mutually beneficial exchanges for re-use of wastes and by-products thus inventing innovative approaches for obtaining raw materials and optimising the value of wastes of their specific processes. In addition, the concept is discussed as a practical approach for “improving the resource effectiveness, reducing the generation of waste and green-house gas emissions by exchange of raw materials, energy, by-products among various processes and industries” (Sun et al., 2017). Thus it became included in the background of strategies for promoting transition to circular economy by promoting the transition of flows of resources through multiple cycles in various sectors and supply chains. The success of industrial symbiosis depends on cooperation of the organisations and synergic opportunities, available in the geographical neighbourhood.

Companies that have applied the business model of industrial symbiosis may reduce production costs and thus achieve economic benefits and, in the meantime, create environmental and social benefits for the entire society (Simboli et al., 2015). In this regard, the industrial symbiosis has been recognised as one of the key strategies that support the transition to circular economy (Lopez et al., 2018). Several studies have revealed that industrial symbiosis may be a useful approach of companies to reduce their CO2 emissions (Sun et al., 2017), which complies with the objectives of the Paris Climate Accords (Nieto et al., 2018).

Conventional methods for assessment of the symbiotic network include assessment of the lifecycle, taking account of the impact on the environment, recycling and re-use of wastes and comparing several referent scenarios. It has always been
focused on reduction of the impact of industrial symbiotic network on the environment in the high-risk business sectors.

**Types of industrial symbiosis**

The concept of industrial symbiosis finds its expression through "eco-industrial parks". The eco-industrial park is characterised as a community of manufacturing enterprises that cooperate with each other in order to effectively share resources (information, materials, water, energy, infrastructure and natural habitat). The collective benefit is economic efficiency and benefits in the context of the environment and local communities. The variety of waste flows and industries characterises also the variety of the types of industrial symbiosis. Chertow (2000) is the first one to deliver a systematic description and categorisation of the industrial symbiosis. She detailed study of 18 potential eco-industrial parks models and proposed taxonomy with five defined types of industrial symbiosis based on exchange of resources:

<table>
<thead>
<tr>
<th>Type of industrial symbiosis</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchange of wastes</td>
<td>Collecting and recycling of waste paper, metals etc.</td>
</tr>
<tr>
<td>Inner utilisation in the framework of one organisation</td>
<td>Treatment of wastewater from production processes and re-use</td>
</tr>
<tr>
<td>External utilisation among organisations – members of a common industrial zone</td>
<td>Waste heat and steam generation</td>
</tr>
<tr>
<td>External utilisation among organisations, outside a common industrial zone, however located geographically close to one another</td>
<td>Various materials</td>
</tr>
<tr>
<td>External utilisation between organisations – connected by a digital platform</td>
<td>That type of industrial symbiosis provides much more opportunities because of the higher number of potential participants</td>
</tr>
</tbody>
</table>

**Analyses of non-hazardous waste - produced and transferred for utilisation in Bulgaria**

The major objective of the statistical studies on produced wastes is to provide information about the quantity of produced waste and waste transferred for utilisation. The review of wastes from production processes in Bulgaria reveals that the mining industry sector occupies the greatest share. The attention has been drawn by the great difference between total waste and waste from mining industry (Figure 1).

![Production wastes, total for the country (Bulgaria), tons](image)

**Fig. 1. Production waste, total for the country (Bulgaria); Source: Bulgarian National Statistical Institute, www.nsi.bg**

Production wastes transferred for utilisation, total for the country (Bulgaria), are presented in Figure 2. The attention has been drawn by the great difference between total transferred non-hazardous wastes and transferred wastes from the mining industry.
Fig. 2. Transferred for utilisation production waste, total for the country (Bulgaria); Source: Bulgarian National Statistical Institute, www.nsi.bg

Analysis of results from the empirical study and a discussion

The present study has analytical and applied character. Its methodological foundations are based on the development of a survey in an on-line format and carrying out an investigation of intentions and opinions of 13 companies of the mineral raw-material sector. The scope of the survey comprises enterprises of different sizes. The persons who took part in the survey occupy positions in the management and they are responsible for making managerial decisions and actively participate in the development and application of strategies and business models. The survey may not pretend for exhaustiveness, even that leading companies from the mineral resource sector in Bulgaria belong to the scope of the surveyed ones. The summaries of the survey and its results are important and indicative for the formulation of conclusions and recommendations and may also be used as a background for future research.

The answers to the query “Are you aware of the concept for an “industrial symbiosis” – a process, by which waste or by-product of a certain industry or industrial process become raw materials for another industry?” provide convincing results that more than 90% of the management of the surveyed companies is definitely aware of the concept. (Figure 3).

More than 90% of the surveyed persons responded positively to the query “Are you aware of real examples from Bulgaria, concerning the “industrial symbiosis” – instead of being thrown away or destroyed, the excessive resources generated by a certain production may be collected and re-directed to be used as a “new” contribution to another production by one or more companies, thus providing mutual benefit or symbiosis”. The attention is drawn by the fact that the share of those, who are not aware of real examples from Bulgaria, related to industrial symbiosis is very low – those are at least 8.3% (Figure 4).
Examples of a successful process in this regard is the collaboration between the ContourGlobal Maritsa East 3 Thermal Power Plant and Knauf Bulgaria, the companies utilise technical gypsum (produced by the sulphur-treatment installations of the thermal power plant) as a raw material for production of gypsum products. The benefits of that good practice are both economic and environmental.

The cooperation between Aurubis Bulgaria and Haidelberg Devnia Cement, and also Holcim Bulgaria and Titan Zlatna Panega Cement is in the same context. The companies utilise fayalite (the main secondary product of the process of copper recovery from copper concentrates) in the construction process.

The last query in the empirical survey marks the intentions of management concerning the participation of the company into a metabolism as “industrial symbiosis”. Seventy five (75) % of the surveyed ones replied positively, 8.3% negatively, and 16.7% consider that industrial symbiosis is not applicable to their business activities. (Figure 5).

The business benefits resulting due to the application of industrial symbiosis are predominantly economical, related mainly to reduction of the cost for waste management and relevant infrastructure. In the context of “green policies”, the environmental benefits are valued more and more – the wastes are utilised as raw materials in other sectors. Care for society and the environment - part of the strategy for corporate social responsibility is another stimulus for companies of the mineral raw material sector (Bakardzhieva, 2010). The major constrains in front the application of industrial symbiosis in Bulgaria are of administrative and economical character. Good communication strategy and coordination among participants is also required. The major emphasis among the barriers is the need of financial instruments, for example for subsidising the treatment of wastes.

Industrial zones and platforms

Industrial zones may be developed as a regional unit, part of a national platform, providing services directly to the participants in the zone.

In Bulgaria, the concept “industrial zone” has not yet obtained a juridical status and zones of that type are formed completely on a regional basis, i.e. in order to provide communal services and infrastructure.

The platforms for industrial symbiosis are among the main instruments for coordinating the connection between consumers and suppliers of by-products or waste flows as well as sources of innovative technologies and expertise. According to a study of wastes produced in the country (Bulgaria), possible business models for waste treatment and studying the options available in the other countries was carried out within the “Solid Waste Reuse Platform for Balkan” Project. The study revealed that those platforms most substantially contribute to industries with a large number of small and medium-size enterprises that have limited time and human resources to identify the potential opportunities for an industrial symbiosis. The implementation of a successful project of that type requires a strategy for development of a platform, technical expertise, mutual confidence and perfect communication (Denkstatt, 2019).

The industrial symbiosis is characterised with a variety, resulting from the variety of the system elements. The companies affiliated to the industrial symbiotic network, usually come from various industrial sectors. Therefore, they produce various types of wastes and require various types of raw materials. Furthermore, those companies may be affiliated to different supply chains and they would not have cooperated with each other had they not participated in the waste exchange. The principle of variety is a basic one for the industrial symbiotic networks because it allows production of various wastes and requires various raw materials within the same industrial symbiotic network (Fraccascia et al., 2017). In fact, the more various companies are included within an industrial symbiotic network, the higher is the opportunity for establishing industrial-symbiotic interrelations and creating a long lasting sustainable system. In spite of the above, “variety of included participations means variety of interests, preferences and values that might be contradicting” (Chertow, 2004). With regard to the above “organisational cultures” of participating companies are different. The models and management styles vary. The more variety is available in the system, the more complicated and more challenging are the efforts for harmonising and making the strategies of specific companies compliant with the entire network strategy” (Baumgartner et al., 2010).

Conclusions and recommendations

The industrial symbiosis has definitely been characterised as a circular business model, the implementation of an industrial symbiosis results in multiple benefits.

Transparency and active dialogue between different stakeholders, organising of information-exchange events, working groups and meetings for exchange of information among the industries are decisively important for the application of innovative technologies, resulting in understanding the benefits of industrial symbiosis.

In the Bulgarian context, to this date, a strong governmental policy is missing to prepare a Strategy for circular economy and a roadmap that will facilitate the transition from linear to circular economy, which involves the application of industrial symbiosis.

Based on this publication, the following recommendations are proposed:
An empirical survey proved that the concept is familiar in the mineral raw-material sector; the management bodies are familiar with the good practices in that aspect and recognise the opportunity to enter into a similar symbiotic network. The potential opportunity for applying such a network has practically been defined, even that this happens mainly in large enterprises of the processing industry.

Elements that will substantially facilitate the establishment of an industrial symbiosis in a national context consist in establishing a national programme or platform for development of industrial symbiosis, mechanisms, supporting the creation of expert groups and scientific projects.

The platforms for industrial symbiosis, which map the enterprises, are the major instrument for exchange of information, coordinating and planning of practical implementation and in this aspect, the establishing of a working structure of that type is especially important. The platforms are discussed as a channel for establishing an effective connection between potential consumers and suppliers of by-products or waste flows, as well as sources of innovative technologies and expertise.

The industrial zones are substantially important for planning of future partnerships in order to apply the industrial symbiosis.

References


MODELLING THE IMPACT OF COAL SEAM METHANE ON THE MONGOLIAN ECONOMY

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ABSTRACT. Energy independence is one of the most important issues for almost every country and the world. Mongolia strives to have various types of energy sources and reduce energy dependence. Energy dependence always influences economic dependence of any country. Utilising its own country’s resources is optimal to reduce energy dependence. In recent years, the Mongolian Government has been encouraging unconventional oil and gas exploration and foreign investment and implementing supporting policies, such as coal bed (seam) methane. As a result of these activities, unconventional oil and gas investment and exploration have been intensified in the last few years in Mongolia, especially during pandemics. There are 32 oil and gas blocks in Mongolia and coal bed methane exploration and foreign investments have been invested in eight blocks. In 2022, some foreign investment companies are going to introduce proven reserves of coal bed methane to the Mongolian Government and Parliament. Therefore, we have to model the positive and negative impacts of coal bed methane on the Mongolian economy and find methods to increase the positive sides. Unfortunately, there is no experience in any situation for unconventional oil and gas exploration, extraction, and field development. Because of it, we have cooperated with Australian scientists and experts and completed some studies for making a model of the impact of coal seam methane on the Mongolian economy. For today’s condition, the Mongolian Government or Mongolian private companies can’t process coal bed methane activities because of lack of capital expenses and experience. To raise the positive impacts of coal bed methane, foreign investment is of course very important. There are some main purposes to model the impact of coal seam methane on the Mongolian economy:

Key words: cost, price, payment, profit, tax.

Introduction

Team of experts considered the data that had been received from operators, and based on this, scoped out three representative asset scenarios for coal bed methane (CBM) business operating in Mongolia. The main purpose of defining three distinct asset scenarios / cases was to provide a sufficiently broad range of projects, in terms of development scale, scope and cost, to represent the potential range of CBM business opportunity in Mongolia. This is relevant from an investor perspective contemplating new business entry into Mongolia and also highly relevant to Mongolian authorities who wish to design their fiscal regime so that it meets a range of needs, some of which are essential and some desirable, depending on the strategic goals of the State, including:

• Attracting sufficient investment and skill sets into the country, if not locally available, not just for the short-term but also for longer-term mutual benefit;
• Promoting economic growth and local employment from construction, infrastructure development and operations;
• Increasing energy independence and energy reliability within Mongolia (Gantumur, 2019); and
• Unlocking stranded resources that can be used domestically, and if sufficient surplus exists, exporting and selling internationally to generate revenue for the State, support the Federal budget and the balance of trade.

Three CBM development scenarios, comprising a Low, Mid and a High Case, were considered to be sufficiently broad to assess and compare fiscal regimes, without being too onerous in terms of the volume of input and output data to be analysed. After consideration of data received from operators the three scenarios or cases were broadly defined as following:

• Low Case: Small scale CBM to liquefied natural gas (LNG) production for transportation fuel to the local market, e.g. as fuel for cars, trains and trucks. This scenario assumed 30-32 Billion standard cubic feet (Bscf) of gas sales from an initial undeveloped resource of about 40 Bscf. Development costs (CAPEX) were assumed to be about $USD 51 million and Exploration and Appraisal (E&A) capital of about $USD 5 million.
• Mid Case: CBM for gas fired power generation for local market base load power at 80 Mega Watts (MW). This scenario assumed about 146 Bscf of sales gas from an initial undeveloped resource of about 188 Bscf. Development costs were assumed to be about $USD 236 million and E&A capital of about $USD 11 million.
• High Case: CBM for pipeline export to an international buyer. This scenario assumed about 1.015 trillion of standard cubic feet of gas (Tscf) of sales gas from an initial undeveloped resource of about 1.48 Tscf. Development costs were assumed to be about $USD 1,656 million and E&A capital of about $USD 44 million.

The discount date is set to 1 January 2021 after the completion of exploration and appraisal programme and at the time when project participants decide whether the investment in project is attractive to progress into development phase. Therefore, negative cash flows from exploration and appraisal costs paid by contractors are sunk and excluded from the net cash flows and net present value calculation. The impact from sunk cost income tax deductible for tax royalty regime and cost recoverable for product sharing contract (PSC) regime is included in the cash flows and net present value calculation. With all three cases the development takes place after the E&A phase sufficiently defines and de-risks the resources, leading to first gas operations around 2024 for the Low and Mid Cases. However, for the High Case, where gas will be exported to international buyers through a pipeline, the first production is estimated to be around 2028 as the project will need finalisation of gas sales and gas transportation agreements to end users via an onshore pipeline constructed and owned by a third party. As with all CBM developments, unlike conventional,
the field appraisal and development continue throughout the operational phase until late field life to maintain plateau production by compensating for the more rapid decline rates and wider geographical footprints typically observed with CBM. All three cases assumed about 22% volume reduction from the initial resource as a result of field fuel usage, CO2 removal, gas shrinkage and other operational related losses. The upstream development scope in all three cases excluded gas processing plant and capital as it was assumed, based on the local market setting, that the gas processing would be handled under a tolling arrangement with a third party. This cost is, therefore, included as part of the field operating expenses (OPEX) assumption. Likewise, the water treatment costs, that are also a typical CBM feature, are handled as an OPEX via a tolling arrangement through a third party plant. In all cases the CBM development scope and costs were limited to the upstream project only. In other words, the fiscal point of sale for the gas would be the field export pipeline flange to one of three potential market entry points. From a fiscal modelling viewpoint, it is very important to be clear about the point of sale, where the gas produced is valued, as that location defines the upstream development scope and costs that are recoverable (for PSCs) or depreciable (for Royalty-Tax Regimes) and the scope and costs that fall outside the petroleum fiscal framework. For the purposes of this exercise and for simplicity the modelling scope encompasses upstream assets to the point of sale as defined below.

1. Low Case: Point of sale would be from the field exit flange / at the inlet flange of the feed line into the small-scale LNG plant.
2. Mid Case: Point of sale would be from the field exit flange / at the inlet flange of the feed line into the power station.
3. High Case: Point of sale would be from the field gas compression and treatment plant exit flange / at the inlet flange to the pipeline connection point.

Methodology

Model inputs estimated capital and operating expenditures for Low Case, Mid Case and High Case were provided by current Operators in Mongolia CBM projects. The Energy team reviewed these cost estimates and made necessary adjustments to normalise the data based on benchmarked information and in some cases to anonymise the data from their sources. All the cost estimates were provided in 2020 real values and then inflated using 2% inflation per annum assumption to the time they were incurred. The basis and the unit cost assumptions for capital and operating expenditures are described in Table 1.

Estimated gas price assumptions were provided by CBM Operators in Mongolia, and like the cost information this was adjusted to normalise prices based on a range of market price ranges provided for each case and anonymise the Operator information. All price estimates were assumed to be 2020 real values and then inflated using 2% inflation per annum assumption. The assumed domestic gas prices and export gas price assumptions are described in Table 2 and are reported as prices per million British thermal units (MMBtu) that converts gas volumes to units of heat.

No analysis has been performed on the gas market or gas market risks as part of this study. The following gas market sectors have been identified (Zoljargal, 2018):

<table>
<thead>
<tr>
<th>Market</th>
<th>Netback Gas Price</th>
</tr>
</thead>
<tbody>
<tr>
<td>Domestic Gas Sales for Low Case</td>
<td>$USD 5.50 / MMBtu</td>
</tr>
<tr>
<td>and Mid Case</td>
<td></td>
</tr>
<tr>
<td>Export Gas Sales for High Case</td>
<td></td>
</tr>
</tbody>
</table>

- Urban Gas Demand. This market comprises supply for residential use for winter heating and gas vehicles. The winter heating demand occurs from October to May, whereas gas demand for gas vehicles would be classified as regular use.
- Industrial Gas Demand. This market comprises industrial and chemical enterprises. The number of users will increase as the economy develops.
- Heat and Power Cogeneration. Currently, all heat and power cogeneration plants in Mongolia are coal fired.

The substitution of coal for gas is possible subject to available and reliable gas supply in sufficient quantities. In addition to the above, there is the potential to supply gas to international markets such as China. Significant gas resources would be required to supply such a market and justify capital investment in facilities and pipelines. For the Low Case, an ex-field delivery price of $USD 5.50 / MMBtu was assumed. With estimated LNG processing and liquefaction fees of $USD 3.0 - 3.5 /MMBtu for LNG (Adam and Garnett, 2021), an assumed distribution fee of $USD 0.75-1.00 /MMBtu (Adam and Garnett, 2021), LNG would be sold to end users at a market price slightly below $USD 10 /MMBtu. At this price level, LNG was considered to be competitive to liquid fuel alternatives, i.e. sufficiently cheaper than petrol for cars or diesel for trucks / trains to incentivise the switch to LNG. For the Mid Case, an ex-field delivery of $USD 5.50 / MMBtu was assumed for gas sold to a power generation plant. At this price level, gas would be competitive to diesel, fuel oil, or even coal if environmental impacts are taken into consideration. For the High Case, an ex-field delivery price of $USD 7.50 /MMBtu was assumed.

### Table 1. Cost assumptions for capital and operating expenditures

<table>
<thead>
<tr>
<th>CAPEX and OPEX Assumptions</th>
<th>Basis ad Unit Costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well and Facility CAPEX</td>
<td>$USD 0.450 MM / well</td>
</tr>
<tr>
<td>Gas Production related OPEX (variable)</td>
<td>$USD 0.050 / Mscf raw gas</td>
</tr>
<tr>
<td>Water Treatment OPEX (variable)</td>
<td>$USD 0.100 /barrel of water</td>
</tr>
<tr>
<td>Workover, Maintenance &amp; Field Operation OPEX</td>
<td>$USD 0.05 MM fixed per year and $USD 150000 per online well</td>
</tr>
<tr>
<td>Gas Processing Tariffs (OPEX)</td>
<td>$USD 0.750 / Mscf raw gas</td>
</tr>
<tr>
<td>Abandonment Cost</td>
<td>6.5 % of well and facility CAPEX to be spent equally 5 years after the drilling campaign</td>
</tr>
<tr>
<td>Exploration and Appraisal</td>
<td>10 % of CAPEX for Low Case 5 % of CAPEX for Mid Case 2.5 % of CAPEX for High Case</td>
</tr>
</tbody>
</table>

### Table 2. Gas price assumptions

- Urban Gas Demand. This market comprises supply for residential use for winter heating and gas vehicles. The winter heating demand occurs from October to May, whereas gas demand for gas vehicles would be classified as regular use.
- Industrial Gas Demand. This market comprises industrial and chemical enterprises. The number of users will increase as the economy develops.
- Heat and Power Cogeneration. Currently, all heat and power cogeneration plants in Mongolia are coal fired.

The substitution of coal for gas is possible subject to available and reliable gas supply in sufficient quantities. In addition to the above, there is the potential to supply gas to international markets such as China. Significant gas resources would be required to supply such a market and justify capital investment in facilities and pipelines. For the Low Case, an ex-field delivery price of $USD 5.50 / MMBtu was assumed. With estimated LNG processing and liquefaction fees of $USD 3.0 - 3.5 /MMBtu for LNG (Adam and Garnett, 2021), an assumed distribution fee of $USD 0.75-1.00 /MMBtu (Adam and Garnett, 2021), LNG would be sold to end users at a market price slightly below $USD 10 /MMBtu. At this price level, LNG was considered to be competitive to liquid fuel alternatives, i.e. sufficiently cheaper than petrol for cars or diesel for trucks / trains to incentivise the switch to LNG. For the Mid Case, an ex-field delivery of $USD 5.50 / MMBtu was assumed for gas sold to a power generation plant. At this price level, gas would be competitive to diesel, fuel oil, or even coal if environmental impacts are taken into consideration. For the High Case, an ex-field delivery price of $USD 7.50 /MMBtu was assumed.
based on an estimated landed gas price in international markets of about $USD 8.50 / MMBtu with $USD 1.00 / Mcf for pipeline transportation fee (Busby et al., 2011). Additional price and cost sensitivities were not conducted for the scope and purposes of this exercise.

The input summaries for each of these cases are presented in Table 3 to Table 5 (Janarbaatar, 2018).

Low Case: Small Scale CBM to LNG Production for Transportation Fuel to the Local Market.
Mid Case: CBM for Gas Fired Power Generation for Local Market Base Load Power at 80 MW
High Case: CBM for Pipeline Export to an International Buyer.

Table 3. Development input summary for low case

<table>
<thead>
<tr>
<th>Development Metrics</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Gas Production</td>
<td>40.6</td>
<td>Bscf</td>
</tr>
<tr>
<td>Total Sales Gas Produced</td>
<td>31.5</td>
<td>Bscf</td>
</tr>
<tr>
<td>Total Water Produced</td>
<td>19.2</td>
<td>MMstb</td>
</tr>
<tr>
<td>Development Wells Drilled</td>
<td>106</td>
<td>#Wells</td>
</tr>
<tr>
<td>Average Recovery Per Well (post fuel+flare use)</td>
<td>0.30</td>
<td>Bscf/Well</td>
</tr>
</tbody>
</table>

Table 4. Development input summary for mid case

<table>
<thead>
<tr>
<th>Development Metrics</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Gas Production</td>
<td>188.2</td>
<td>Bscf</td>
</tr>
<tr>
<td>Total Sales Gas Produced</td>
<td>146.1</td>
<td>Bscf</td>
</tr>
<tr>
<td>Total Water Produced</td>
<td>89.1</td>
<td>MMstb</td>
</tr>
<tr>
<td>Development Wells Drilled</td>
<td>492</td>
<td>#Wells</td>
</tr>
<tr>
<td>Average Recovery Per Well (post fuel+flare use)</td>
<td>0.30</td>
<td>Bscf/Well</td>
</tr>
</tbody>
</table>

Table 5. Development input summary for high case

<table>
<thead>
<tr>
<th>Development Metrics</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Gas Production</td>
<td>1477.6</td>
<td>Bscf</td>
</tr>
<tr>
<td>Total Sales Gas Produced</td>
<td>1147.0</td>
<td>Bscf</td>
</tr>
<tr>
<td>Total Water Produced</td>
<td>700.2</td>
<td>MMstb</td>
</tr>
<tr>
<td>Development Wells Drilled</td>
<td>3872</td>
<td>#Wells</td>
</tr>
<tr>
<td>Average Recovery Per Well (post fuel+flare use)</td>
<td>0.30</td>
<td>Bscf/Well</td>
</tr>
</tbody>
</table>

Mongolia CBM projects currently operate under Production Sharing Contracts (PSC) with cost recovery and profit split between Government and Contractors (Otto et al., 2006). The revision of Mongolia Petroleum Law in 2014 simplifies certain fiscal terms including the elimination of income tax, dividend withholding tax, and value added tax and customs tariff. Key Government take fiscal terms for CBM projects are negotiable with the authorities for each individual Operator and potentially for each individual license. In accordance with the 2014 Petroleum Law, royalty ranges from 5 % to 10 % of gross revenues. The cost recovery limit and profit sharing for the Government are negotiable on project-by-project basis. The profit sharing for Government is not graduated but applied on a production rate threshold. For the analysis, royalty rate is assumed to be 7.5 % as the midpoint of the 5-10 % range (Dugervar, 2018). The Energy team has reviewed the cost recovery limit and profit sharing for Government assumptions made by Operators and made necessary adjustments to normalise and anonymise the fiscal terms (Janarbaatar, 2018). Signature bonus and production bonuses are not included in the analysis. Table 6 summarises the fiscal terms assumptions (Gen, 2018).

Table 6. Summary of Mongolian PSC terms (Binderman, 1999; Smith, 2013)

<table>
<thead>
<tr>
<th>Fiscal terms</th>
<th>Petroleum Law</th>
<th>Assumptions in the analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Royalty</td>
<td>5 % - 10 %</td>
<td>7.5 %</td>
</tr>
<tr>
<td>Cost Recovery Limit</td>
<td>For CBM - to be determined</td>
<td>70 %</td>
</tr>
<tr>
<td>Profit Sharing for Government</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-1 Million m³/day</td>
<td></td>
<td>30.0 %</td>
</tr>
<tr>
<td>1 – 2 Million m³/day</td>
<td></td>
<td>32.5 %</td>
</tr>
<tr>
<td>2 – 3 Million m³/day</td>
<td></td>
<td>35.0 %</td>
</tr>
<tr>
<td>3– 4 Million m³/day</td>
<td></td>
<td>37.5 %</td>
</tr>
<tr>
<td>&gt;4 Million m³/day</td>
<td></td>
<td>40.0 %</td>
</tr>
<tr>
<td>Tax Rate [2]</td>
<td>Exempted</td>
<td>0.0 %</td>
</tr>
<tr>
<td>Dividend Withholding Tax</td>
<td>Exempted</td>
<td>0.0 %</td>
</tr>
<tr>
<td>VAT ad Customs Tariff</td>
<td>Exempted</td>
<td>0.0 %</td>
</tr>
<tr>
<td>Contractor Participating Interest</td>
<td>100 %</td>
<td>100 %</td>
</tr>
<tr>
<td>Signature Bonus</td>
<td>As proposed by Contractor</td>
<td>Not included</td>
</tr>
<tr>
<td>Production Bonus</td>
<td>As proposed by Contractor</td>
<td>Not included</td>
</tr>
</tbody>
</table>

Model Inputs for Low, Mid and High Cases (Adam and Garnett, 2021) are presented in figures from 1 to 6.

Conclusion

In all cases, the Royalty-Tax regime yields significantly higher undiscounted cashflows and rates of return to investors, compared to the PSC regime.

- Conversely, in all cases Government cashflow and discounted cashflow are higher for all cases under the PSC regime. However, when Government take is too high it does not encourage new investments, few or no projects will be developed resulting in sub-optimal Government take. The fiscal regime should be designed to encourage new investments which will result in multiple project developments and optimised Government cashflow at an aggregate level.

- From an Investor / Operator / Contractor perspective, projects exemplified by the Low Case could not be supported under the PSC and yielded only marginally economic results under the Royalty-Tax terms (Figure 1, Figure 2). The impact of this is that under the PSC regime there will be less gas supply that can be developed compared to a Royalty-Tax regime. Natural resource opportunities tend to follow distributions where there are far more “low case” opportunities than “high case” ones. The fiscal model chosen influences how many opportunities are economic. Ultimately, lower supply will tend to cause higher gas prices and, thus, fewer opportunities for economic development.
• Similarly, marginal projects under a PSC framework, as demonstrated by the Mid Case would struggle to pass through the internal decision-making process for most companies unless returns could be supported by further technical improvement and/or commercial improvement and/or some type of fiscal incentive (Figure 3, Figure 4). The Mid Case project yielded economic results under the Royalty-Tax regime terms and could proceed under this fiscal regime.

• Projects like the High Case could proceed on the economic merits, but the reality is that investment decisions are not made on economic merits alone (Figure 5, Figure 6). For most successful businesses, a range of decision criteria are used for their investment decisions. Decisions of this scale, or requiring entry into a new country, would normally be supported by a comprehensive risk and opportunity assessment that is both quantitative and qualitative in nature, i.e. would include a range of non-technical risks.

• Compared to the PSC regime, the Royalty-Tax regime treats smaller scale, lower value projects less harshly than larger scale, more profitable projects. At the same time, the Royalty-Tax regime still provides a “good” level of return to the Investor / Operator / Contractor for those large-scale, more profitable cases.

• For the larger scale projects exemplified by the High Case, the returns are high under both regimes, with better after-Tax returns for the Operator under the Royalty-Tax regime at all discount rates considered. The high returns for such a large-scale venture would be considered commensurate with the higher capital exposures (i.e. larger amounts of capital placed at-risk) involved, the longer lead

Fig. 1. Upstream Development Capital – Low Case

Fig. 2. Upstream Operating Costs
timings to first production, the commercial complexity of the project and higher risks in a new resource play in a new business environment.

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Gantumur S., 2019. The geothermal energy study in Arkhangai province, Proceeding of International Conference on Oil and Gas Conference, 19, Part 1, 179-186.


PHYTOREMEDIATION OF POST-MINING DISTURBED LAND

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ABSTRACT. Sustainable land application in post-mining areas is an essential ecological issue, connected with disturbed areas, pollution of heavy metals, etc. The current research studies opportunities for phytoremediation of lands disturbed by copper mining. Environmental state and soil conditions are examined. Analyses show that soils are weakly acidic, with a low concentration of total nitrogen, a very high concentration of K_2O and P_2O_5, and arsenic above permissible values. The research determines phytostabilisation as a more reliable method for phytoremediation of disturbed lands in this case. The appropriate species for phytostabilisation have been studied. Based on the analysis of data, climate, and soil conditions, it is determined that tree species of four genera show the best ability for phytoremediation in this type of terrain: Populus, Betula, Acer, Salix. Afforestation schemes and possible methods for biomass treatment are proposed.

Keywords: copper mining, reclamation, phytoremediation, phytostabilisation

Introduction

Mining and mining waste management contamination of soils with heavy metals and metalloids (HMM) poses a serious risk to human health and the environment (Kostadinova et. al., 2016; Todorova et al., 2019; Malinova et al., 2022) and thus provokes significant interest in developing technologies for their remediation, ecosystem restoration (Zukova – Aleksandrova and Mitkov 2018; Petrov, 2019), and sustainable use. Although there are many physical and chemical technologies proposed for the removal of HMM from soils, serious attention is paid to the possibility of phytoremediation due to the economic efficiency and environmental friendliness of the method.

Bioremediation uses the natural ability of some species of plants and microorganisms to extract, transform and inactivate HMM from the soil, based on the normal vital functions of organisms (Vasilev 2005; Bezlova 2016). Through their metabolic processes, plants and microorganisms use pollutants as a source of energy, and in most cases reduce their concentration to safe levels (Vasilev, 2005; Akhtar, 2013). For successful phytoremediation, the selected species must be tolerant to pollutants, must accumulate large amounts of biomass and finally - biomass at the end of the process should not be hazardous waste. The main phytotechnology used in the remediation of soils contaminated with HMM are phytoextraction, phytostabilisation, and phytoevaporation (Angelova et al., 2004; Vasilev, 2005; Emamverdian et al. 2018; Yadav et al., 2017, 2018).

In phytoextraction, plants remove heavy metals through their root system, accumulating them in their roots or transporting them to their aboveground parts (stems and leaves) (Cardwell et al. 2002; Kramer, 2005; Goolsby and Mason 2016; Emamverdian et al. 2018). Phytoextraction is a slow process of extracting heavy metals, applicable to soils with surface layer contamination and heavy metals that are not in high concentrations (Vasilev, 2005; Meyerholt 2013; Budzyńska et al., 2013).

In phytostabilisation, the contaminants are immobilised in the root system by absorption into the roots of the plants or by precipitation in the rhizosphere, reducing the mobility of pollutants (Llugany 2012; Ali et al., 2013; Mani et al., 2013). Phytostabilisation has been developed as a technology based on the experience of restoring industrially damaged soils around old mines or metallurgical plants, which were often due to the high content of HMM and poor physicochemical characteristics of the soil, where vegetation is virtually absent (Chang et al., 2002; Fitz, 2002; Vasilev, 2005).

The present study aims to investigate the possibilities for phytoremediation of soils contaminated with heavy metals and metalloids because of past copper production, determine the appropriate method of phytoremediation, determine the appropriate species based on literature research and analysis of soils and environmental conditions in the area and prepare a plan for afforestation and application of amendments such as fertilizers.

Methods and materials

Study area

Soil samples were taken from sites contaminated because of mining activities in the Zlatitsa-Pirdop valley. This site will be used for forestry purposes after the reclamation. The study area is in forest areas at an altitude of 734 m. 6 sample subareas (SS) have been identified - sample subarea (SS) 1, SS 2, and SS 3 are industrial sites, and SS 4, SS 5, and SS 6 are old embankments because of past activities (Figure 1.).

Fig. 1. Part of the sample places
Materials

To achieve the objectives of the study, soil samples were taken from six sample areas - industrial sites and old embankments resulting from copper mining in the past. The sampling was performed according to standard BDS 17.4.5.01-85 “Nature protection. Soil. General requirements for sampling”.

Methods

To determine the soil conditions, their physicochemical properties were studied. Soil reaction (pH) was measured potentiometrically following ISO 10390. The humus content was measured by Tyurin titrimetric (TT) method. Total nitrogen in the soil was determined by the Kjeldahl method, assimilable forms of potassium and phosphorus - by the method of Petko Ivanov. The total content of Fe, Mn, Pb, Zn, Cu, Cd, As, and total S was determined by dissolving the samples in aqua regia followed by ICP-OES.

Results

Analysis of soil condition

According to the studies of soil samples (presented in Table 1), the soils are slightly alkaline and neutral.

Table 1. pH value and content of nutrients and humus

<table>
<thead>
<tr>
<th>Sample subareas (SS)</th>
<th>SS 1</th>
<th>SS 2</th>
<th>SS 3</th>
<th>SS 4</th>
<th>SS 5</th>
<th>SS 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.9</td>
<td>8.0</td>
<td>6.5</td>
<td>6.9</td>
<td>6.8</td>
<td>7.0</td>
</tr>
</tbody>
</table>

The value of pH is due to conducted methods of remediation of soils, involving liming. In SS 1 and SS 2 the soils are slightly alkaline. Under these conditions, alkaline earth carbonates are present in the soil, especially those of calcium. They are characterised by unfavourable conditions for plant nutrition due to the excess of basic cations and the lack of microelements. The soils in SS 3, SS 4, SS 5, and SS 6 have a neutral pH. They have a significantly lower amount of alkaline earth carbonates; nutrition is more balanced and has a prerequisite for optimal agrochemical mobility of soil elements (Malinova, 2010; Petrov, 2019), pH values are a prerequisite for the use of phosphorous fertilisers, as they are only applicable in alkaline environments.

In the studied samples, the fertility of the soils was determined by humus content and the content of total nitrogen, assimilable forms of phosphorus and potassium (Figure 2). Soil fertility is important for the further selection of tree species (Petrova et al., 2019; Petrov, 2019), as well as for determining the necessary ameliorants. The classification of soils by the content of nutrients and humus is made according to scale introduced by Penkov (1996). The analysed soils are characterised by a small stockpile except for SS 2, in which a high stockpile is observed. In terms of humus content, the soils in the different sample areas vary from poor humus (SS 4), medium humus (SS 3, SS 5, SS 6), and rich humus (SS 1) to abundant humus (SS 2). According to the results of the analysis, fertilisation with nitrogen fertilisers should be envisaged, except for SS 2. In all samples, the content of assimilable forms of phosphorus is very high. Potassium reserves vary from very high (SS 4, SS 5) to very large (SS 1, SS 2, SS 3, SS 6).

The content of Fe, Mn, Pb, Zn, Ni, Cu, As, and total S were determined in the studied soils (Table 2 a, b).

Table 2. a) Concentration of Fe, Mn, total S, mg/kg

<table>
<thead>
<tr>
<th>SS</th>
<th>Fe</th>
<th>Mn</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/kg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SS 1</td>
<td>29397</td>
<td>391</td>
<td>10</td>
</tr>
<tr>
<td>SS 2</td>
<td>40037</td>
<td>397</td>
<td>4560</td>
</tr>
<tr>
<td>SS 3</td>
<td>26189</td>
<td>582</td>
<td>25751</td>
</tr>
<tr>
<td>SS 4</td>
<td>27923</td>
<td>395</td>
<td>12590</td>
</tr>
<tr>
<td>SS 5</td>
<td>29657</td>
<td>417</td>
<td>1174</td>
</tr>
<tr>
<td>SS 6</td>
<td>31034</td>
<td>429</td>
<td>1526</td>
</tr>
</tbody>
</table>

b) Concentration of Cu, Pb, Zn, Ni, Cd, As and their maximum permissible concentrations (Order 3/2008)

<table>
<thead>
<tr>
<th>SS</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Ni</th>
<th>Cd</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/kg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SS 1</td>
<td>532</td>
<td>45</td>
<td>76</td>
<td>17</td>
<td>1</td>
<td>109</td>
</tr>
<tr>
<td>SS 2</td>
<td>1232</td>
<td>135</td>
<td>190</td>
<td>18</td>
<td>2</td>
<td>303</td>
</tr>
<tr>
<td>SS 3</td>
<td>714</td>
<td>56</td>
<td>116</td>
<td>8</td>
<td>1</td>
<td>102</td>
</tr>
<tr>
<td>SS 4</td>
<td>62</td>
<td>81</td>
<td>75</td>
<td>14</td>
<td>1</td>
<td>59</td>
</tr>
<tr>
<td>SS 5</td>
<td>249</td>
<td>106</td>
<td>79</td>
<td>14</td>
<td>1</td>
<td>42</td>
</tr>
<tr>
<td>SS 6</td>
<td>120</td>
<td>85</td>
<td>74</td>
<td>16</td>
<td>1</td>
<td>76</td>
</tr>
<tr>
<td>MPCs</td>
<td>500</td>
<td>500</td>
<td>600</td>
<td>25</td>
<td>10</td>
<td>40</td>
</tr>
</tbody>
</table>

Fig. 2. Content of a) humus content and content of total nitrogen; (b) content of P₂O₅ and K₂O in soil samples

The calculated coefficients (H_{HPC-pollutant}) showing the exceedances of the maximum permissible concentrations (Order 3/2008) for the pollutants exceeding the norms are presented in Table 3.
According to the results, the iron content is below the average for soils in the country - 3.8% (Gyurov, 2015) except for PP 2. The manganese content falls in the range typical for soils - 200 -1000 mg/kg (Kabata-Pendas, 2011), but it is below the national average - 1000 mg/kg (Malinova, 2010). The content of Pb, Zn, Ni, and Cd does not exceed the MPCs for the respective element. The results of the soil samples show that most of the sample areas are lightly polluted (SS 4, SS 5, SS 6), moderately polluted (SS 1, SS 3) or dangerously contaminated with arsenic (SS 2), and practically unpolluted concerning copper (SS 4, SS 5, SS 6), slightly polluted (SS 1, SS 3) or moderately polluted (SS 2). The high levels of arsenic found in the studied samples are a prerequisite for impaired soil mineralization and its ability to self-clean, and the development of vegetation, because of toxic effects on microbial flora (Kabata - Pendas, 2011; Yankova, 2016).

Table 3. Coefficients showing the exceedances of the MPC for arsenic and copper

<table>
<thead>
<tr>
<th>Sample subareas</th>
<th>SS 1</th>
<th>SS 2</th>
<th>SS 3</th>
<th>SS 4</th>
<th>SS 5</th>
<th>SS 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMPC-As</td>
<td>2.73</td>
<td>7.59</td>
<td>2.57</td>
<td>1.49</td>
<td>1.07</td>
<td>1.90</td>
</tr>
<tr>
<td>HMPC-Cu</td>
<td>1.06</td>
<td>2.46</td>
<td>1.42</td>
<td>0.13</td>
<td>0.50</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Soil analysis shows that phytoremediation is possible. They have a neutral pH, at which plant nutrition is close to balanced (Malinova, 2010). The studied soils are also rich in potassium and phosphorus, as well as well-stocked with humus. The content of copper in them is according to the permissible norms or exceeds the MPC up to 2 times. The content of arsenic suggests that methods should be sought for its removal or stabilisation in soils. Toxic levels (Penkov, 1996) of total S are reported.

Characteristics of the ecological condition of the region

The climate in the region is a temperate-continental climate (Sabev and Stanev, 1963), with mild winter and cooler summers. The northeast wind is predominant for the region - 25% on average for the year. The annual amount of precipitation is 617-618 mm. The snow cover lasts about 100 days. According to the Soil-geographical zoning of Bulgaria, the territory and the studied sites fall into the South Bulgarian xerothermal soil zone and the Mountain soil zone. Because of the little width in the studied area, we cannot talk about soil diversity in the area around the sample subareas, as this area has long been anthropogenically affected. In terms of floristics, the region falls within the floristic regions of Western Sredna Gora and Central Stara Planina according to the floristic zoning of the country. The natural vegetation is represented by pure and mixed oak, hornbeam, and beech forests (Serafimova et al., 2019).

Land use in the sample areas is mainly for forestry. Ecosystems are negatively affected by mining activities - many old embankments have been located. That is the reason for the change in vegetation. Black pine (Pinus nigra) and acacia (Robinia pseudoacacia) are also induced in the local flora during the reclamation of disturbed areas. Erosion was also found in the areas subject to sampling. In combination with the challenging natural type of restoration of vegetation, it threatens the protection and restoration of ecosystems (Djingova et al., 1993; Bancheva-Preslavskia, 2017, 2018, Zukova-Aleksandrova, Mitkov, 2018, 2019).

Phytoremediation of the sample areas

Determination of phytoremediation method

Successful phytoremediation is a complex of interactions between soil, pollutant, and plants, and depends on several factors: the degree of soil contamination, the bioavailability of the pollutant(s), and the ability of plants to capture, absorb and accumulate the pollutant(s). In the present study, two approaches for phytoremediation of disturbed terrains are considered - phytoextraction and phytostabilisation. Phytoextraction is the most effective method of phytoremediation but does not apply to specific soil conditions. According to the literature, the method applies to soils with low concentrations of pollutants (Meyerholt, 2013), and as can be seen from the analysis of soil samples, the copper content exceeds 2 times the MPC and arsenic up to 7.6 times (SS 2). Another prerequisite for rejecting the method as applicable to the specific conditions is the possibility of the formation of a large amount of waste biomass with a high content of arsenic and the need to treat them as hazardous waste.

In soils contaminated with As and Cu phytostabilisation is a recommended method (Zhao et al. 2016; Yang et al. 2016), as the method results in a change in soil chemical composition induced by the presence of the plant itself and leads to immobilisation of pollutants in plant roots (Zhang et al., 2009).

Under specific soil conditions (hazardously contaminated with arsenic soils) phytostabilisation is also considered the more appropriate method. For successful remediation, the appropriate species for its implementation have been studied. The species are selected according to the requirements of the method (to select plant species with dense root systems to prevent leaching of pollutants (Singh, 2012), tolerant or resistant to pollutants - copper and arsenic, in this case, to have rapid growth and high biomass production, non-edible. Climatic and soil conditions in the area, natural vegetation, and land use in the areas around the test areas - namely as forest areas are also considered.

Selection of plant species

In the literature, several species have been reported as phytostabilisers applicable to specific climatic and soil conditions - the members of the family Violaceae, Rhododendron tomentosum and Veronica beccabunga (Bergqvist and Greger 2012), Salix alnifolia (Otones et al., 2011), Lupinus albus et al., 2006, Festuca rubra (Radziemska et al., 2017), Hypericum perforatum, Teucrium orientale, Phleum pratense (Ghazarian et al., 2018). For the application of this method, some authors believe that there are more appropriate tree plant species due to the large amount of biomass formed by the deep root system. Species of the Salicaceae family are used for this purpose. The combination between representatives of the genus Salix and Populus is suitable, such as Populus nigra, P. alba, P. tremula, Populus euramericana, Salix alba, Salix purpurea, Salix caprea, (Borgegard and Rydin, 1986; Punshon et al., 1995). Proven stabilisers of arsenic are members of the genus Acer - A. pseudoplatanus and A. platanoides (Budzynska et al., 2019).

In the present case, the use of tree species is considered the better alternative due to the following arguments: i) land
use in the area - the sample areas are in forest areas; ii) high concentrations of pollutants - tree species would speed up the cleaning process due to the large amount of biomass they form, in the deep root system.

Based on the ecological characteristics of the area, the analysis of the condition of the soils in the studied areas, the location of the studied sites in forest areas, the purpose of their future use, and the literature review for phytoremediation of the studied sample areas it is appropriate to use the species: Populus tremula L., Betula pendula Roht., Acer platanoides L., Salix alba L. The characteristics of the species determine them as suitable for phytoremediation in the region, as they are naturally distributed in the region (Asyov et al., 2012) and are proven stabilisers of relevant pollutants. Betula pendula Roht is a tree species that accumulates a large amount of biomass, has a well-developed root system with well-developed lateral roots, can graze on extremely infertile soils; stabilises Cd > Mn > Zn > Pb > Cu > Ni > Fe. Populus tremula L. is a fast-growing tree species with great adaptability to soil conditions; stabilises Cd, Cu, Pb, Zn, Ni, and Cr. Acer platanoides L. is a tree species with a highly developed root system, tolerant to different soil types. It stabilises As, Cu, Pb, Ti, and Zn. Salix alba L is a fast-growing tree species with a large central root and strongly developed dense lateral roots that are not demanding to soil fertility, it stabilises As, Cd, Cu, Zn, Sb (Porter et al., 1975; Pajević et al., 2016).

**Planting schemes of the species**

It is envisaged that the average norm of saplings will be over 600 pieces/da due to unfavourable conditions because of high concentrations of arsenic in the soil. The planting schemes that are proposed assume optimal vegetation development and maximum results from the applied reclamation. Distance between individuals should be 0.65 m for Populus tremula L., and 0.80 m for the other species. The distance between the rows should be 1.30 m. They are presented in Figure 3.

**Fig. 3. Planting schemes**

**Appropriate ameliorants**

Increasing the effectiveness of phytoremediation can be achieved through appropriate ameliorants. Soil analysis suggests the use of nitrogen fertilisers, as soils are poor in total nitrogen. It is recommended to apply ammonium nitrate twice after rainfall, in the spring immediately, and during the growing season, so that there are no losses, there is a longer-lasting effect, and to accelerate plant growth.

Fertiliser application rate is 7 kg/acre. The other necessary ameliorant is superphosphates. Phosphorus fertilisers are important for the faster rooting of plants and support their overall growth and development, and on the other hand, they help neutralise arsenic in soils. It is recommended that they be imported in the autumn before phytoremediation. Fertiliser application rate is 11 kg/acre.

**Treatment of generated biomass**

Proper management of waste biomass resulting from phytoremediation is extremely important, as it poses a risk of re-contamination of the environment with heavy metals. Among the most widely used methods for biomass treatment are composting, incineration, pyrolysis, liquid extraction, energy use through combustion or gasification, biofuel production, or landfill (Śyc et al., 2016). The conditions described above do not suggest that the resulting biomass will contain arsenic and copper in increased amounts, as they will be stabilised in the rhizosphere. Studies show that the content of arsenic in the aboveground parts of the genus Salix is in the order of 1%. It was also found that the metalloid accumulates in the roots of wood species of the genus Populus, and less in their aboveground parts (Pajević et al., 2016).

Under these conditions, composting and compaction are good alternatives for the treatment of waste biomass, which has been reported by several authors (Kumar et al., 1995, Raskin et al., 1997, Garbisu et al., 2001). Composting can significantly reduce the volume of green waste, with the additional positive effect of reducing transportation costs to hazardous waste disposal facilities (Blaylock and Huang, 2000).

According to the Bulgarian legislation (Ordinance on separate collection of biowaste and treatment of biodegradable waste, in Art. 3 (1)), it is permissible “Composting on-site” of own biowaste in an amount not exceeding 10 m³/y compost, which is carried out directly from households and other sites, and the resulting compost is used at the place of formation only for own needs.

For the present case, it is recommended to collect waste biomass (leaves, branches, dried saplings) once a year. Before composting, the biomass must be tested for heavy metals and metalloids and pre-analysed for C and N content so that the amounts can be dosed correctly to achieve an optimal C/N ratio at the beginning of the composting process. According to a C/N ratio calculation, a recipe is made for the type and quantities of waste biomass to be placed in a bowl. Composting should be done in the following sequence: shredding of biomass, alternating spreading of fragmented branches, tops, leaves, etc. in a certain order in a layer 15 cm high, and laying a layer of fresh grass or other biowaste containing mainly nitrogen in a layer of 5 cm, forming a pile with dimensions - width 1.20 m, height 1-1.20 m, dew and periodic mechanical inversion - 3 to 5 times per week for the first 21 to 28 days and bowl height <1.3 m. The resulting compost needs to be sieved and its properties tested so that its future application can be determined.

**Conclusion**

As a result of the study of good practices for phytoremediation of soils contaminated with copper and arsenic and the analysis of soil samples, we can conclude that a phytoremediation is a possible approach to the restoration of these areas.

The soils have a neutral pH, medium stock of humus, and high content of phosphorus and potassium. The heavy metals and metalloids studied, except for arsenic, do not exceed the
MPC. Arsenic levels exceed the MPC, which makes phytostabilisation a more reliable method under specific conditions. Phytostabilisation is expected to lead to the immobilisation of the pollutant in the rhizosphere and reduce the possibility of generating waste biomass with hazardous properties.

The following plan has been developed for phytoremediation:
- Afforestation with four tree species known in the literature as phytostabilisers: Populus tremula L., Betula pendula Roht., Acer platanoides L., Salix alba L.
- Due to soil conditions (arsenic content above the MPC) it is recommended that the number of tree species should be over 600 per acre. Distance between individuals should be 0.65 m for Populus tremula L., and 0.80 m for the other species. The distance between the rows should be 1.30 m.
- The low nitrogen content determines the application of ammonium nitrate - twice in the spring before and during the growing season with a fertiliser application rate of 7 kg/acre.
- Before afforestation, it is planned to apply superphosphates with a fertiliser application rate of 11 kg/acre.
- It is recommended that the resulting biomass be composted on site.

It is important to note that phytostabilisation is not a technology for real cleaning of contaminated soils, but a successful strategy for stabilisation (inactivation) of TMM, which are potentially dangerous to humans and the environment. In situ inactivation of pollutants prevents their further spread and this reduces the impact on the site and adjacent ecosystems. Therefore, in the long run, the monitoring of pollutants is an integral part of the successful management scheme of phytostabilisation.

Afforestation of the selected species will take place in the spring of 2022. It is planned to sample the soil and the resulting biomass at the end of the growing season. A positive effect is expected to be reported after the third year.

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HAUL ROAD DESIGN OPTIMISATION APPROACH FOLLOWING TECHNOLOGICAL CONSTRAINTS IN OPEN-PIT MINING

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ABSTRACT. Modern mining practices rely to a great extent on the application of numerical methods for establishing design alternatives, leading to significant economic benefits. In the current article mine haul road design and construction are treated as two interconnected problems – 1) selection of a suitable optimisation approach for haul road design and selection of an optimal pit design solution; 2) selection of a suitable technology for haul road construction. Based on previous research, the main factors which determine haul road design feasibility have been identified. They are used for the purpose of establishing the key performance parameters which define the optimality of a haul road design solution. An optimisation problem is defined, which relies on different design solutions and the alternatives for a feasible ultimate pit design. Solutions of this optimisation problem are expected to maximise the mine’s long-term profit. Furthermore, statistical parameters were obtained providing insight into affirming why a certain design solution is more dominant to others in a more robust way.

Key words: haul road design, haul road construction, open-pit mining

Introduction

The design of an efficient haul road for an open-pit mine is one of the most essential elements of pit design problems. It is of utmost importance to optimise transportation costs, due to the high amount of costs in relation to the structure of total operational costs. Different authors point out that haulage operations can contribute from 49% up to 70% of the total operational costs (Mohutsiwa and Musingwini, 2015; Nancel-Penard et al., 2019). In addition, assuming different haul road design parameters can affect the ultimate shape of the pit, which can lead to the excavation of additional volumes of overburden and waste material or to cease the access to certain volumes of ore. Nonetheless, different approaches to haul road and pit design aim to maximise the overall revenue for the mining operation, utilising different numerical methods (Aleksandrova, 2007; Akay et al., 2013; Baek and Choi, 2017; Morales et al., 2017; Nancel-Penard et al., 2019; Yarmuch et al., 2020). As efficient as they could be, in many cases certain parameters (e.g. number of pit entry points, suitable road grade, etc.) may not be established in a solution from such algorithms. However, they can be used as guidelines for determining which design alternatives or solutions provided by a certain algorithm are feasible and therefore suitable for the establishment of the ultimate pit design with respect to technological constraints and operational safety requirements. Furthermore, the haul road design problem is treated as two separate problems, regarding ex-pit road design and ramp design (Yarmuch et al., 2020). Nonetheless, the results provided from each of the two solutions are related to one another and the overall optimality of each design alternative. In addition, both solutions should meet the constraints, deriving from the technological parameters, capabilities and size of the equipment. Therefore, the overall haul design problem can be divided into two interconnected problems – 1) selection of an appropriate optimisation approach for haul road design and selection of an optimal pit design solution; 2) selection of a suitable technology for haul road construction and maintenance. R. Thompson et al. (2019) have established an interactive approach to the design phase and the operational phase of a haul road operation (Figure 1).

Furthermore, the author has also established a trend line, based on previous observations, which shows that the utilisation of more formal design methods reduces significantly the possibility for accidents. Hence, in order to achieve a reliable and realistic solution for an optimisation problem, an overview of the capabilities and limitations of different optimisation approaches has to be made. This would require an overview of the technological constraints for road construction, as well as the haul road and pit design parameters which provide a guideline for optimisation algorithms and other design methods.

Fig. 1. The interconnectivity between structural, functional and maintenance design (Thompson et al., 2019)
Haul road and pit design parameters overview

In terms of design parameters, in-pit and ex-pit haul road construction relies on the same principles: slope angle and bench height are dependent on the physical and mechanical properties of the rock types, road width directly corresponds to width of the truck model utilised and the work shift output of the pit (Zlatanov and Aleksandrova, 2005; Aleksandrova and Zlatanov, 2008; Aleksandrova, 2013; Koprev, 2015). Figure 2 represents the basic design of a trench and a “semi-trench” which corresponds to the geometry of an in-pit ramp design between the topography and a bench or between two sequential benches at an initial stage of mining (Koprev, 2016).

Fig. 2. Basic design of a trench (left) and “semi-trench” (right), depending on topography (Aleksandrova, 2013)

For each segment of a haul road the length of the road (L) can be calculated by the formula (Aleksandrova, 2013):

\[ L = \frac{H}{i} \]  

(1)

H – elevation passes or pit bench height, m;  
i – road slope grade, %.

A key requirement is that the road curvature must respect the turning radius of the utilised trucks. The road’s curvature radius (R) is calculated in the following manner (Thompson et al., 2019):

\[ R = \frac{V^2}{127(U_{\text{min}} + e)} \]  

where V – vehicle speed (km/h);  
e - super-elevation rate (m/m);  
U_{\text{min}} - coefficient of lateral friction supply.

Road width (W) as another crucial parameter can be calculated by either way (Baek and Choi, 2017; Koprev, 2017):

\[ W = (1.5 \cdot L + 0.5) \cdot X \]  

(3)

where L – number of lanes;  
X – width of haulage equipment, m.

\[ W = n \cdot W + 2. \cdot y + x \cdot (n - 1) \]  

(4)

where x – safety distance between the trucks carrybacks, m;  
y – distance between truck wheel and road end, m

\[ y = 0.5 \cdot x + 0.5 \cdot 0.005 \cdot V^2 \]

Earthworks regarding haul road construction involves (drilling and blasting), loading, hauling, unloading and bulldozing. However, in terms of ex-pit road design and construction, the problem is regarded mainly as an earthwork allocation problem, where the optimisation objective is to partition the optimised cut-to-fill-assignments in different earthwork sections with minimal movement between them (Figure 3).

Fig. 3. Cut and fill road construction modelling with earth allocation optimisation problem (Ji and Borrmann, 2014)

Ramp design problems have a similar ultimate goal – rock mass allocation must be performed in the most cost-effective manner. However, in order for this to be achieved, the task is interpreted as a problem for obtaining an optimal ultimate pit design and a maximum sum of cash flows after obtaining a set of pushbacks leading to the ultimate pit. Hustrulid et al. (2013) point out that the main purpose of the ramp design is to provide access to the complex geometry of the ore body. It is also established that the location of the ramps can significantly change the overall slope angle of the pit and therefore influence the overall stripping ratio of the pit, as well as the profitability of the mining operation due to different volumes of rock mass (Figure 4).

Fig. 4. Open-pit design parameters (Grenon et al., 2011)

In addition, the ultimate pit depth and topography can significantly influence the total length of the pit ramp segments, as well as the number of times the haul road spiral intersects a profile view of the pit’s slope (n). In such sections of the pit slope the overall slope angle is influenced by the number of intersections, which can be determined by the formula (Aleksandrova, 2013):

\[ n = \frac{L}{0.5 \cdot (P_b + P_s)} = \frac{K \cdot H}{i \cdot (P_b + \pi \cdot h \cdot \cotg \alpha)} \]  

(5)

where L – total in-pit haul road length, m;  
P_b – pit bottom contour length, m;  
P_s – pit surface contour length, m;  
K – haul road extension factor;  
H – pit depth, m;  
h – bench height, m;  
\alpha – slope angle, °.

However, this formula works best for cases where only one rock type zone is present, and the ultimate pit shell can be approximated to a truncated cone. It has been stated that the actual value for n (as a real number) can be up to 15% higher than its true value, which from a practical standpoint provides a satisfactory level of accuracy. The overall slope angle can be calculated by applying the formula (Koprev et al., 2015).
where $\beta$ – overall pit slope angle, °; 
$B$ – berm width, m; 
m – number of benches; 
other symbols as described above.

To sum up, the main aspects, which must be considered for the design phase of the haul road include:

- **Maximum revenue for ultimate pit design.** Pit design should not cease access to valuable sections of the ore deposit and provide as much access to the ore body as possible. At the same time, the pit design should minimise waste volumes as much as possible in order to reduce unnecessary mining costs and the need for clearing more spaces for storing waste rock.

- **Minimum costs for the transport of rock mass throughout the life of mine.** Long-life haul roads are preferable than short-life roads as this reduces overall road construction costs and operating costs (Attkinson, 1992). Therefore, roads exiting from pit walls are more feasible. However, it should be kept in mind that this criterion is site specific due to the crusher location and the ore and waste dump locations (Hustrulid et al., 2013; Paricheh and Osanlo, 2016; Liu and Pourrahimian, 2020). Haulage costs are also related to the number of access points to the pit. More access points may provide greater flexibility, however, this may not be the best cost-effective solution (Hustrulid et al., 2013).

- **Maximum level of safety.** A crucial part of creating a safe work environment is the avoidance of areas or design parameters which can compromise the slope stability (Attkinson, 1992). In terms of operational safety, additional switchbacks may provide feasible solutions, however, it is established that switchbacks tend to slow traffic, cause greater tyre wear and various road maintenance problems (Hustrulid et al., 2013). Furthermore, sight distance is obligatory to be significantly higher than truck stopping distances, which requires a larger vertical radius both for in-pit and ex-pit haul roads.

- **Maximum productivity.** This is related to the road width which would minimise traffic congestion (Attkinson, 1992). This also corresponds to the required truck hours for the mining equipment, which can further minimise the fleet size and therefore minimise investment and operational costs. However, it should be kept in mind that excess road width may also improve slope stability, but it reduces the undiscounted profit of the mine.

- **Minimum level of ecological impact.** This aspect is related to maintaining a low artificial footprint on the surrounding areas in terms of noise levels, dust generation, CO₂ emissions, as well as the possibility of waste rock utilisation for bed materials.

All the aforementioned factors are related to the key design parameters of the haul road design both for ex-pit and in-pit conditions. At the same time, both cases of in-pit and ex-pit road constructions aim at minimising haul distances, due to its direct impact on the operational costs during the life of mine. Hence, different approaches regarding this optimisation problem have been established which target complementing minimal investment costs with minimal operational costs whenever possible.

### Existing algorithms and approaches

Even though the construction of ex-pit haul roads and in-pit ramps have a similar technological process, earthworks sequencing and optimal design parameters estimation, the design process regarding optimisation techniques and suitable approaches can vary significantly. The reason for this separation of different approaches is that each optimisation problem focuses on a specific set of parameters which can be calculated by repeating operations representing different scenarios.

#### Ex-pit haul road design algorithms

This part of the optimisation problem is related to other civil engineering problems such as the construction of roads belonging to the state road network, roads serving the forest industry as the construction of these types of roads require lower stripping activities, compared to the mining industry. Therefore, certain approaches have already been established which provide practical solutions.

#### Road Layout simplification algorithms

The application of line simplification algorithms is performed to minimise transport distances via eliminating vertices for achieving an appropriate road design. Apart from applying a conventional Euclidean Distance method a number of times for the road layout, line simplification algorithms can also be applied, which include the following algorithms: Wall-Danielson (Wall and Danielson, 1984), Latecki-Lakamper (Latecki-Lakamper, 1999), Douglas-Peucker (Douglas and Peucker, 1973), Visvalingam-Whyatt (Visvalingam and Whyatt, 1993) and the Zhao-Saalfeld algorithm (Zhao and Saalfeld, 1997). Out of the listed above, the Douglas-Peucker algorithm has been successfully used in a haul road optimisation problem for open-pit mines as a complementary approach to the design problem (Baek and Choi, 2017). Mondal et al. (2015) develops a bi-level programming model for the optimisation of the horizontal alignment in a specified corridor as well as a globally optimal vertical alignment. Casal et al. (2017) have presented a method for the optimisation of horizontal alignment roads (which are composed of circular curves and tangent line segments joined by means of transition curves). As simple as it may be, this approach provides a basis for minimising operational costs due to the minimisation of haul distances.

#### Discrete optimisation techniques

On the other hand, discrete optimisation techniques have been widely used to design roads in forest operations. One of the most applicable approaches consists in dividing the terrain into cells and then associating with each cell a certain set of nodes to represent the directions in which the cell can be accessed.

Digital elevation models allow the discretisation of the terrain in cells with a cubic shape or with different sizes for their three dimensions. In addition, unlike geological block models, cells in earth allocation problems could have smaller sizes without the concern of decreasing the accuracy of estimations, as ex-pit road cell databases do not need to have attributes regarding ore grades or other geochemical contents. However, a smaller cell size and a higher number of neighbours would increase the resolution of the model, but
makes it harder to solve (Heinimann et al., 2003; Stückelberger, 2008).

The raster-based least cost path analysis (LCPA) method has mainly been used to analyse and determine the optimum path at the local scale such as paths for a pipeline, material transportation at a construction site and last but not least mining haul road design (Baek and Choi, 2017). The LCPA method consists of two steps: 1) the cost of passing every cell from the origin is calculated based on the cost surface data, which contains the cost of passing each cell, and these values are recorded in every cell and 2) the least-cost path is derived using the back-link mechanism based on the calculation results of the accumulated travel cost recorded in all cells.

In-pit ramp design methods

Block model approach

The block modelling approach is one of the most powerful and successfully implemented methods for solving mining problems, regarding the optimisation of the pit contour, establishing pushbacks and scheduling mining operations, whenever a vast number of technologically feasible solutions exist. The principles of applying directed graphs are similar to the ones implemented in ex-pit haul road optimisation algorithms. Figure 5 represents the set of blocks which are responsible for maintaining the technological feasibility of the ultimate pit contour by removing blocks, which are standing in potential ramps locations.

![Fig. 5. Ramp set, blocks b and b' selected as accesses: green blocks are in the path, yellow blocks have to be removed due to precedence constraints; (left) Resulting profile after ramp construction (right) (Nancel-Penard et al., 2019)](image)

Depending on the position of the two blocks the slope and width of the ramp can be adjusted for obtaining the potential ramp location candidates. The objective function of this algorithm is to maximise the economic value of the removed blocks from the block model (including the blocks representing the ramp entry and exit points). The nodes of each cell are then connected to the nodes in the neighbourhood cells, creating a graph that represents possible paths. Thus, grade constraints, as well as constraints regarding the turning radius of the ramp can be incorporated into the problem.

This approach has several modifications of the algorithm used for obtaining an optimal solution in the search space of the directed graph, as more notable solutions are provided by Morales et al. (2017), Nancel-Penard et al. (2019), Yarmuch et al. (2020), etc.

Limitations of existing algorithms and methods

Ex-pit haul road algorithms

Existing ex-pit haul road algorithms have some limitations regarding the identification of a best road solution – some authors formulate the objective function to solve the earthworks allocation problem (which corresponds to minimising investment costs for road construction), while others focus on the objective to minimise the complexity of the polyline to achieve a smaller travel distance (which serves as a tool for minimising operational costs). Raster-based approaches and LCPA algorithms provide a good basis for practical and future design work, which solve both problems. However, as a directed graph problem, they face the problems all similar problems have – when the complexity of the graph is increased, heuristic methods are required to be utilised in order to obtain a solution, in terms of a practical time constraint. Another alternative is to simplify the problem and neglect certain parameters which may lead to conflicting solutions, when ultimately all design parameters are considered by the designer. Undoubtedly, the solutions from the different types of computer-based approaches can be time-saving, to some extent they remain suboptimal, considering the vast number of factors required for simultaneous optimisation. As in every optimisation problem, in rare cases not every constraint can be met, thus some constraints have to be relaxed, which leads to relying on the parameters in the objective function. Nonetheless, they are irreplaceable tools to engineers and are further developed to exceed their current limitations.

In-pit ramp methods

In-pit methods have similar problems to the ones mentioned for ex-pit haul road algorithms. Although in-pit design algorithms based on block models can produce an optimal solution from a wide range of calculated pit models, the main limitation of such approaches is the inaccuracies of the calculated result from the block model to the actual geometry of pit design. Adjustment of block sizes of a block model in order to meet the adequate size suitable for ramp geometry parameters (width, length, slope) require tampering with the block model ore grades for each sub-block inside a parent-block which may lead to minor but nonetheless false interpretations of the spatial distribution of ore grade and other attributes from the geospatial model. And last but not least, approaches based on directed graph representations of the ultimate pit contour rarely establish an early estimation of haulage costs (other than the presupposed haulage costs in the sum of mining costs), deriving from ramp lengths besides the total profit value of the ultimate pit. Therefore, most authors focus mainly on optimising the total profit of different ultimate pit scenarios and neglect the true nature of operational costs. Truly, they can be calculated in a more robust way during pushback definitions and scheduling.

Scope of study

As it has already been pointed in the overview made, different optimisation problems inevitably disregard certain parameters, which are further calculated for the post-optimisation solutions during the design process and the determination of an optimal pushback sequence. In cases where solutions from optimisation algorithms are well segregated such an approach is truly accurate, as the assumed inaccuracies are irrelevant. Based on a brief
overview of the existing optimisation approaches, the current paper’s main focus is on the in-pit ramp design problem as a potential starting point for minimising the search space for the optimisation algorithms. In addition, this approach could provide an interpretation of a potential threshold value which the absolute difference between the optimised parameters (in-pit haul distance, total profit, stripping ratio, etc.) of the design solutions from optimisation algorithms should exceed, in order for them to be ranked in a more reliable way. Therefore, cases which have subtle differences between the key performance parameters have to be further investigated and ranked when reducing them to a detailed ultimate pit design.

Case study

Aim of the study

This paper aims to propose an optimisation approach, which utilises an already established result from a certain block model optimisation solution for the development of a realistic open-pit design surface. The proposed steps could be repeated a number of times, depending on the desired number of candidates for a specific design alternative and the desired level of confidence one wants to achieve. The result from these actions allows the user to make an initial assessment of the feasibility of each ultimate design result in a more robust way by including an approximate preliminary calculation of haulage costs before introducing pushbacks. Afterwards, each ultimate design is compared to all other results, which leads to the establishment of the most feasible design or to the point where certain optimisation parameters need to be relaxed and more ultimate pit designs need to be investigated.

Preliminary information

Automated pit design provides the instantaneous creation of technologically feasible pit designs after the optimisation process has been completed by a certain algorithm. This approach complements block model approaches and serves as a basis for further pit design adjustments to be generated in each pit for the sequence of mining operations. This approach may be more time consuming than heuristic approaches based on algorithms solving directed graphs as it requires some manual work, but it provides a more accurate way for obtaining volume calculations and design solutions which fully respect the technological constraints of an open pit mine, e.g. the curvature radius, the super-elevation of the in-pit haul road, the need of horizontal sections between ramps on consecutive benches, etc.

A case study is presented here treating the haul road optimisation problem as part of the ultimate pit design optimisation problem. The current gold deposit, used for this case study is suitable for mining and extraction for a period of 35 years with an annual ore output of 500000 t/a. The whole procedure of obtaining a “fine-tuned” ultimate pit design is presented in Figure 6.

Initially by using the block model of the deposit an economical model was obtained using a standard methodology of including mining costs for ore and waste material as well as processing costs for the ore. The exact values for these costs cannot be provided due to commercial confidentiality. However, an approximate value for mining costs can be provided which was estimated to be approximately 48 $/t regarding ore.

This includes mining costs, waste rock costs, processing costs, administrative costs, royalties and selling costs. The assumed price of Au was 58 $/g. Furthermore, for confidentiality reasons the obtainable profit for the ultimate pit design candidate used in this paper are provided as standardised values depending on the maximum profit value out of all the considered alternatives.

Apart from the overlying clays above the ore zones, for the most part rock types for the deposit remain consistent with an average density of approximately 2.7 t/m³ for siltstones with a high density of quartz inclusions. These conditions are suitable for establishing a bench height of 15 m for the ultimate pit design with a slope angle for each bench of 60°. The bench width was assumed to be 6 m.

Following the well-established approach of obtaining a solution of the extent of the open-pit mine, the Lerch-Grossman optimisation algorithm was utilised for the economic model, providing an ultimate pit shell. For the sake of establishing a technologically feasible pit contour the overall slope angle was utilised as a constraint for the algorithm. However, in order to achieve a more realistic pit contour depending on the pre-supposed ramp grade and the number of intersections per profile line, an ultimate pit shell was generated, by utilising an overall pit slope angle of 42°. By applying formulae (5) and (6) the following results were established:

\[ n = \frac{L}{0.5 \cdot (P_o + P_r)} \]

\[ n = \frac{L}{0.5 \cdot (P_o + P_r)} \]

Two intersections were assumed for the following formula:
\[ \beta = \arctg \frac{10.15}{20.2 + 6.7 + 10.15 \cdot \cotg 60^\circ} \approx 42^\circ \] (9)

After obtaining a pit shell from the Lerch-Grossman algorithm, three alternative approaches can be undertaken for establishing the candidate locations for ramp locations and design parameters depending on the design direction: 1) pit bottom – pit contour (up); 2) pit contour – pit bottom (down) or 3) combined approach. Each of the three approaches is valid. For the sake of simplicity, the first approach was utilized in this case study due to the shape of the ore body, which is more suitable for the pit bottom – pit contour approach. Hence, a small volume of ore could remain unextracted with this approach at the lower benches of the pit, compared to the other two alternatives.

Following the steps of Nancel-Penard et al. (2017) and D. Liu et al. (2020), initially 4 candidate points were considered for the pit bottom string for each of the two assumed cases of road grade (8% and 10%), which lead to the consideration of more candidate points during the process. Figure 7 represents the pit bottom string, the 4 initial candidate points and the 4 secondary candidate points for the second iteration. Afterwards, each scenario provides an end-point for the uppermost ramp, intersecting the topographic surface and the pit contour. A manual approach was utilised to connect the pit’s entrance point to the state road network as well as the same entry point to the waste dump location.

Fig. 7. Candidates for ramp starting point located on a search space of the pit bottom string

Road width was calculated to be approximately 20 m, while the turning radius was assumed to be 25 m for a maximum speed of 20 km/h and superelevation of 3%. Coefficient of lateral friction was assumed to be 0.16 (Koprev et al., 2017). The key performance parameters were considered for the choice of a dominant design solution. Initially the considered parameters for this analysis included:

1) **volume of minable ore** – volume of ore with grade higher than the cut-off grade, which remains inside the ultimate pit surface;

2) **volume of minable waste** – volume of waste which is to be mined for establishing the shape of the ultimate pit surface;

3) **stripping ratio** – stripping ratio value for the pit surface with a value lower than the maximum allowable stripping ratio;

4) **total undiscounted profit** – overall financial results of the mining operation, calculated by the designed ultimate pit model and according to the pushback direction;

5) **total area of the pit contour** – this area can be interpreted as the disturbed area for reclamation, after the end of LOM (life of mine);

6) **total amount of CO₂ truck emissions** – ecological footprint of the mining operation;

7) **total amount of truck hours** – parameter used for determination of total fleet size, which indirectly corresponds to operational safety.

However, several of the aforementioned parameters are collinear as some of them are extended variants of the other. Therefore, in terms of feasibility of the mining operation the parameter **total undiscounted profit** is used for ranking all design alternatives. The ecological impact of the mining operation is described with the **total amount of CO₂ truck emissions**. The total amount of truck hours is collinear with the amount of CO₂ emissions and therefore is neglected as a key parameter. The total area of pit contours differs up to 10 decares which is not negligible, however the total pit area was used as a complementary parameter.

To establish a better understanding of the feasibility of each design alternative, apart from the general approach of calculating the undiscounted profit for the ultimate pit based on the block model, an approach similar to the one of Yarmuch et al. (2020) has been utilised. The total amount of ore and waste volume which is situated on each bench is assumed to be transported from the pit through the ultimate ramp design configuration. It is well-known that that ramps and in-pit haul roads are not constantly available or existing during the life of mine, which inevitable would complicate the problem. Nonetheless, two principal pushback scenarios exist, which provide an insight into other more realistic scenarios (Figure 8).

The picture on the right represents a conventional pushback scenario, while the one on the left shows the bench-by-bench pushback scenario, which is not a realistic one. However, it has been established in previous research by other authors as an approach for a similar problem (Anachkov and Konstantinov, 1985).

Fig. 8. Pushback configurations for open-pit mining. Bench-by-bench (left). Realistic pushbacks (right)

Nonetheless, in terms of haul distances it needs to be further investigated whether this approach provides a pessimistic or optimistic estimation of operational costs. For the current case study, it was assumed that the bench-by-bench pushback approach is in action and the volume for each bench is hauled from its respective depth.

After ranking all design alternatives on the calculations made only for the initial 4 candidate points for the start of ramp, the secondary 4 candidates were included in the analysis. This applies for both scenarios of the haul road slope grade. This step is conducted in order to limit the search space and look for other potential solutions. This approach can be done any number of times, but for the sake of simplicity it has been done only twice for this case study.

Last but not least, all design alternatives from the considered scenarios are ranked according to their total undiscounted profit and total amount of CO₂ truck emissions.
Results

Two scenarios have been considered (clockwise and counterclockwise ramp directions) for two design alternatives (8% and 10% ramp grade). The same starting points for the locations of the candidate ramp designs were used for both scenarios and slope grade. Table 1 shows the results for the clockwise scenario.

Table 1. Scenarios for 10% grade of ramps

<table>
<thead>
<tr>
<th>Candidate</th>
<th>Scenario</th>
<th>Ore Volume [Mt]</th>
<th>Waste Volume, [Mt]</th>
<th>Stripping Ratio</th>
<th>In-pit Haul Distance [m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CW</td>
<td>17.07</td>
<td>19.94</td>
<td>1.17</td>
<td>1862.6</td>
</tr>
<tr>
<td>2</td>
<td>CW</td>
<td>17.02</td>
<td>19.58</td>
<td>1.15</td>
<td>1812.2</td>
</tr>
<tr>
<td>3</td>
<td>CW</td>
<td>16.98</td>
<td>19.76</td>
<td>1.16</td>
<td>1761.8</td>
</tr>
<tr>
<td>4</td>
<td>CW</td>
<td>16.91</td>
<td>19.89</td>
<td>1.18</td>
<td>1741.6</td>
</tr>
<tr>
<td>5</td>
<td>CW</td>
<td>16.88</td>
<td>19.68</td>
<td>1.17</td>
<td>1638.7</td>
</tr>
<tr>
<td>6</td>
<td>CW</td>
<td>16.96</td>
<td>19.76</td>
<td>1.17</td>
<td>1614.9</td>
</tr>
<tr>
<td>7</td>
<td>CW</td>
<td>16.96</td>
<td>19.93</td>
<td>1.18</td>
<td>2069.5</td>
</tr>
<tr>
<td>8</td>
<td>CW</td>
<td>16.96</td>
<td>20.52</td>
<td>1.21</td>
<td>1869.3</td>
</tr>
</tbody>
</table>

* CW – clockwise, CCW – counterclockwise

Table 2. Scenarios for 8% grade of ramps

<table>
<thead>
<tr>
<th>Candidate</th>
<th>Scenario</th>
<th>Ore Volume [Mt]</th>
<th>Waste Volume, [Mt]</th>
<th>Stripping Ratio</th>
<th>In-pit Haul Distance [m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CW</td>
<td>17.08</td>
<td>21.37</td>
<td>1.25</td>
<td>2035.3</td>
</tr>
<tr>
<td>2</td>
<td>CW</td>
<td>17.07</td>
<td>21.21</td>
<td>1.24</td>
<td>1939.5</td>
</tr>
<tr>
<td>3</td>
<td>CW</td>
<td>17.03</td>
<td>21.52</td>
<td>1.26</td>
<td>2010.7</td>
</tr>
<tr>
<td>4</td>
<td>CW</td>
<td>16.98</td>
<td>21.75</td>
<td>1.28</td>
<td>2121.7</td>
</tr>
<tr>
<td>5</td>
<td>CW</td>
<td>16.96</td>
<td>21.65</td>
<td>1.29</td>
<td>2246.6</td>
</tr>
<tr>
<td>6</td>
<td>CW</td>
<td>16.99</td>
<td>21.92</td>
<td>1.29</td>
<td>2421.1</td>
</tr>
<tr>
<td>7</td>
<td>CW</td>
<td>16.98</td>
<td>21.72</td>
<td>1.28</td>
<td>2464.7</td>
</tr>
<tr>
<td>8</td>
<td>CW</td>
<td>16.97</td>
<td>21.90</td>
<td>1.29</td>
<td>2220.0</td>
</tr>
</tbody>
</table>

* CW – clockwise, CCW – counterclockwise

As it can be observed, different locations of the candidate points can lead to a change of the overall pit shape, as well as the in-pit haul distance. Therefore, in order to evaluate properly each design alternative, haul costs must be recalculated for each designed pit with respect to the established in-pit haul distance.

The hourly fuel consumption (FC) (L/h) was established using Hays (1990) model by applying the formula:

$$ FC = \frac{CSF \cdot P \cdot LF}{FD} \quad (10) $$

where CSF - the engine-specific fuel consumption at full power (0.213 – 0.268 kg/kWh); P - power (kW), LF - engine load factor; FD - the fuel density (0.85kg/l for diesel).

Values of engine load factor are given by Kecojevic and Komljenovic (2010), as follows:

- Low: 20%-30% (Continuous operation at an average gross weight less than the recommended. Excellent haul roads. No overloading, low load factor.)
- Medium: 30%-40% (Continuous operation at an average gross weight approaching the recommended. Minimal overloading. Good haul roads, moderate load factor.)
- High: 40%-50% (Continuous operation at or above maximum recommended gross weight. Overloading. Poor haul roads, high load factor.)

Figures 9-12 show that optimality of a candidate pit can change with the methodology utilised for calculation of the undiscounted profit. The in-pit haul distance result neglects ex-pit roads and therefore overestimates the calculated value for the undiscounted profit. In contrast, the in-pit and ex-pit haul distance result in a more realistic estimation of the undiscounted profit with respect to haul distances and ore and waste volumes inside the pit contour.
In addition, in this case study the in-pit haul distance result correlates highly with the combined haul distance result ($R^2=0.8269$ for the 10% road grade and $R^2=0.892$ for the 8% road grade design alternative). This can be attributed to the shorter ex-pit haul distances compared to the in-pit roads, which leads to a higher level of significance for the in-pit haul road design alternatives in terms of the ultimate pit design.

Although, certain values for the estimated profit of the post-optimisation designed pit result are very close to the combined haul distance approach, a low level of correlation is observed between the two data sets. Therefore, the undiscounted profit, calculated by the in-pit and ex-pit combined haul distance is assumed to be the more accurate performance parameter, following an approach similar to the one established by Yarmuch et al. (2020):

$$CO_2 = FC \cdot CF$$

where $FC$ - diesel fuel consumption (L/h), $CF$ - the conversion factor.

The conversion factors of $CO_2$ emission for diesel fuel are calculated using the following dependencies (Kecojevic et al., 2010):

$$CF = CC \cdot 10^{-6} \cdot 0.99 \cdot (44/12)$$

where $CC$ - carbon content for diesel fuel (g/L) 0.99 - the oxidation factor.

Data, provided by Kecojevic et al. (2010) was used to calculate the $CO_2$ emissions for the CAT 772 truck model. It was assumed that fully loaded trucks have high engine load for 10% ramps, medium load for 8% ramps and low load for empty trucks moving downslope. Values for the total amount of $CO_2$ emissions were standardised using the following equation:

$$X_{st} = \frac{X_{min}}{X_i}$$

A similar approach was used for standardising the values for the undiscounted profit:

$$Y_{st} = \frac{Y_i}{Y_{max}}$$

As key performance parameters, $CO_2$ emissions are required to be minimised, while the undiscounted profit should be maximised. Therefore, all standardised variables have a maximum value of 1, which is considered to denote each design alternative which is the most optimal regarding both parameters. The values for the key performance parameters are represented for the Clockwise scenario shown in Table 3. Results from both scenarios and design alternatives regarding candidate points have been presented on Figures 13-14.
For a design to be optimal, if possible, both curves have to reach a value of 1 simultaneously.

Table 3. Clockwise scenario standardised performance parameters (grade: 10%)

<table>
<thead>
<tr>
<th>Candidate</th>
<th>Scenario</th>
<th>Area [dka]</th>
<th>Standardised CO₂ emissions</th>
<th>Standardised undiscounted profit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CW</td>
<td>173.1</td>
<td>0.7800</td>
<td>0.9820</td>
</tr>
<tr>
<td>2</td>
<td>CW</td>
<td>173.5</td>
<td>0.7846</td>
<td>0.9731</td>
</tr>
<tr>
<td>3</td>
<td>CW</td>
<td>177.0</td>
<td>0.8478</td>
<td>0.9834</td>
</tr>
<tr>
<td>4</td>
<td>CW</td>
<td>179.1</td>
<td>0.8439</td>
<td>0.9665</td>
</tr>
<tr>
<td>5</td>
<td>CW</td>
<td>178.1</td>
<td>0.9461</td>
<td>0.9865</td>
</tr>
<tr>
<td>6</td>
<td>CW</td>
<td>173.4</td>
<td>0.9614</td>
<td>0.9910</td>
</tr>
<tr>
<td>7</td>
<td>CW</td>
<td>170.9</td>
<td>0.6750</td>
<td>0.9615</td>
</tr>
<tr>
<td>8</td>
<td>CW</td>
<td>173.5</td>
<td>0.7646</td>
<td>0.9731</td>
</tr>
</tbody>
</table>

Results regarding the counterclockwise scenario are shown in Figures 15 and 16, as well as on Table 4.

Table 4. Counterclockwise scenario standardised performance parameters (grade: 8%)

<table>
<thead>
<tr>
<th>Candidate</th>
<th>Scenario</th>
<th>Area [dka]</th>
<th>Standardised CO₂ emissions</th>
<th>Standardised undiscounted profit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CW</td>
<td>179.5</td>
<td>0.8696</td>
<td>0.9931</td>
</tr>
<tr>
<td>2</td>
<td>CW</td>
<td>173.5</td>
<td>0.9004</td>
<td>0.9953</td>
</tr>
<tr>
<td>3</td>
<td>CW</td>
<td>180.9</td>
<td>0.8680</td>
<td>0.9901</td>
</tr>
<tr>
<td>4</td>
<td>CW</td>
<td>183.3</td>
<td>0.8378</td>
<td>0.9841</td>
</tr>
<tr>
<td>5</td>
<td>CW</td>
<td>185.2</td>
<td>0.7842</td>
<td>0.9777</td>
</tr>
<tr>
<td>6</td>
<td>CW</td>
<td>189.2</td>
<td>0.7096</td>
<td>0.9704</td>
</tr>
<tr>
<td>7</td>
<td>CW</td>
<td>189.9</td>
<td>0.7032</td>
<td>0.9693</td>
</tr>
<tr>
<td>8</td>
<td>CW</td>
<td>187.5</td>
<td>0.8048</td>
<td>0.9803</td>
</tr>
</tbody>
</table>

Therefore, it can be established that candidate 8 from the Clockwise scenario (Grade: 10%) has optimal performance parameters and therefore has to be chosen as the ultimate pit for this analysis. A close result is achieved by candidate 6 from the Counterclockwise scenario (Grade: 10%).

In both cases the exit point is from the side of the ex-pit crusher location and opposite to the waste dump location. In addition, the total amount of CO₂ truck emissions also seems to resemble a strong linear relationship with the total undiscounted profit. This can be explained by the fact that in open-pit mining a large percentage of the operational costs is attributed to haulage operations. This statement also applies in this case study, e.g., for the different scenarios of the open-pit mine, haulage costs vary between 50 and 70% depending on the ultimate pit design and volumes of ore and waste for different scenarios. Therefore, reducing transportation costs can contribute to the undiscounted profit of the mine, while at the same time the CO₂ emissions from truck operations can be reduced.
Figure 18 shows trend lines for both ramp grade scenarios, which prove that the undiscounted profit is strongly dependent on in-pit haul road length. Furthermore, the relationship remains rather consistent for all design alternatives, which leads to the conclusion that the undiscounted costs for the ultimate pit design are related strongly to in-pit haul distance. However, one should keep in mind that the trend line serves only as a general interpretation of the problem and not as a guideline for determination of the undiscounted costs via the in-pit road length. Although in rare cases, there could be a high value for $R^2$, the estimated values are not consistent throughout all design alternatives. The reason for that deviation is that the ultimate pit design also affects the overall sum of the total costs.

Fig. 18. Correlations between in-pit haul length and standardised undiscounted profit

The Mean Average Error (MAE) of the in-pit Haul Road Length was estimated to be approximately 55 m for a 10% ramp grade and 49 m for an 8% ramp grade when solving the equations of their respective linear regression models. Therefore, the MAE is the threshold value which the difference between each two performance parameters of each two design alternatives must exceed for them to be ranked in a proper way.

If another approach is considered – to predict the undiscounted profit for each design via the haul distance length, the MAE value is 885 500 USD for a scenario with a 10% ramp grade and 676 205 USD for a scenario with an 8% ramp grade.

The distribution of the prediction error was estimated for the scenarios with 10% grade. A null-hypothesis of its normality was made with $\alpha=0.05$ assumed. It proved out to be close to a normal one, by performing a Shapiro-Wilk test, which obtained a p-value of 0.786 (Figure 19).

Therefore, a confidence level can be assumed for further ranking future designed alternatives. Using the standard deviation of the error values, the following intervals can be defined:
- 95% level of confidence: $[-2\sigma, +2\sigma]$ ($\pm$ 139.4 m);
- 99% level of confidence: $[-3\sigma, +3\sigma]$ ($\pm$ 209 m).

Hence, depending on the level of confidence one wants to achieve regarding project alternatives, this is the value the differences of the optimised parameters of the design solutions or algorithm-based solutions should exceed. Furthermore, the profitability of the pit can be calculated in a similar manner.

Fig. 19. Normal Q-Q Plot of prediction error distribution of in-pit total ramp length

Conclusions

The current paper proposes a simple approach for haul road design optimisation, which can serve as a basis for the future implementation of algorithms in a tight search space. Rather than using a tree-based block model search approach, the use of 32 automatically designed ultimate pit candidates has not only provided a basis for determining the most feasible way of establishing a ramp design. It has also provided insight into the accuracy and limitations of other optimisation techniques achieving the same or a similar result. Last but not least, a threshold value was established based on the Mean Average Error (MAE), which provides a basis for ranking design alternatives or post-calculation algorithm-based solutions. Furthermore, for greater confidence certain intervals can be defined which provide a certain level of confidence for the future work of designers and programmers when indirectly using a certain parameter for the prediction of another one for more complex profit calculations. In addition, in order to obtain a more robust way of ranking project alternatives, one should know that pushback scenarios have to be included in future research on this topic, so that the change of haulage distances during the LOM is accounted for.

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MEASURING THE INSULATING RESISTANCE IN NETWORKS WITH ISOLATED STAR CENTRE CONTROLLED BY AN AZUR DEVICE

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ABSTRACT. The AZUR apparatus is intended to control the insulating resistance in mine networks with an isolated star centre. The indication of the measured insulating resistance is realised by a pointer meter with a reversed nonlinear scale, which makes it difficult to read. The methodology for the development of an analogue converter is considered here, which linearises the non-linear characteristic current-resistance and, together with a light indicator, the device allows for more accurate and easy reading. An analysis of the error and the measurement range is made.

Keywords: insulating resistance control, mine power networks, measuring analogue converter.

Introduction

The insulating resistance control apparatus in networks with an isolated star centre is designed to create a stable constant operational voltage Uref on the general insulating resistance between the phases and ground. The diagram and the coupling of the apparatus are not subject of this paper.

The simplest AZUR equivalent circuit, on the basis of which the characteristic has been analysed, is given in Figure 1.

![Fig. 1. Equivalent circuit for measuring the insulating resistance in AZUR](image)

The milliamp meter measures the current I, which depends on Rins while its scale, highly non-linear and reverse, is divided into segments in kΩ. The AZUR apparatus is often mounted in an explosion protected casing and the slightly illuminated appliance is observed through a thick glass, which makes it difficult to read the insulating resistance. In addition, the accuracy is unsatisfactory – there is about 10% relative error.

The present paper aims to describe a non-linear analogue converter, which allows the insulating resistance Rins to be transformed into voltage E, which is strictly proportional to it, measured by a digital voltammeter with a LED display. The number of the display is equal to the value of Rins, in kΩ.

First stage - Block I

The first stage of the converter is the AZUR device itself, in which the milliamp meter is replaced by one resistance with an accuracy of 1%, Rm = 100 Ω.

Figure 2 presents Block I, in which the input value is the insulating resistance Rins, and the output value is the drop of voltage over Rm → Ur = 100-I. The resistance Rm is selected with a small value compared to the other resistances in the circuit, so that it does not significantly affect the measured current.

![Fig. 2. Block I, input value Rins - insulating resistance, output value Ur - voltage over Rm](image)

The current I is determined by the circuit in Figure 1 and given as:

\[ I = \frac{160}{20 \cdot 10^3 + 200 \cdot 10^3 \cdot R_{ins}} \]  

(1)

The contour resistance is made up of a Rins connected in parallel to 200 kΩ plus 20 kΩ. The operative voltage UOP = 160 V is stabilised. The Ur voltage is a non-linear decreasing Rins function that is close in shape to a hyperbola. When the input value, the argument of the Rins function grows, the Ur function decreases according to the nonlinear dependence (1).

Let's now set the boundaries of change of Rins and Ur.

The scope of Rins is set from 20 kΩ to 200 kΩ. Resistance below 20 kΩ cannot be measured as AZUR switches off the power supply upon deterioration of the insulating resistance up to 20 kΩ.

At \( R_{ins} = 20 \text{kΩ} \)

\[ U_R = U_R^0 = \frac{100}{20 \cdot 10^3 + 200 \cdot 10^3} \cdot \frac{160}{20 \cdot 10^3} = 0.419 \text{V} \]  

(2)

At \( R_{ins} = 200 \text{kΩ} \)

\[ U_R = U_R^{200} = \frac{100}{20 \cdot 10^3 + 200 \cdot 10^3} \cdot \frac{160}{200 \cdot 10^3} = 0.133 \text{V} \]  

(3)

The change of Ur is equal to

\[ \Delta U_R = U_R^0 - U_R^{200} = 0.419 - 0.133 = 0.286 \text{V} \]  

(4)

The transfer function of Block I
is graphically presented in Figure 3.

The transmitting function of Block I

Second stage - Block II

The purpose of Block II is to convert the decreasing $U(R_{\text{ins}})$ function into an increasing one $U(R_{\text{ins}})$ by amplification, inverting and summing up. It consists of an amplifier with a gain $k$, source of constant voltage $U_0$ and an adder. The functional diagram of Block II is shown in Figure 4.

The output voltage $U$ should be normalised. As $R_{\text{ins}}$ increases ten times from an initial value (20k) to a final one (200k), hence $U$ should increase 10 times accordingly. The change interval of $U$ is determined to be from 1 V to 10 V, i.e. $\Delta U = 9$ V

Next, the gain $k$ and the $U_0$ value are determined. Since $U_R$ is an input voltage and $U$ is an output voltage for Block II

$$k = \frac{\Delta U}{U_R} = \frac{9}{0.286} = 31.5$$

(5)

![Fig. 4. Functional diagram of Block II](image)

$$U = U_0 - kU_R$$

(5')

The initial value of $U$ is 1 V.

$$I = U_0 - kU_{20} = U_0 - 31.5 \times 0.419 = U_0 - 13.2$$

(6)

The final value of $U$ is 10 V.

$$10 = U_0 - kU_{20} = U_0 - 31.5 \times 0.133 = U_0 - 4.2$$

(7)

From (6) and (7) the following value is obtained for $U_0$

$$U_0 = 14.2 \text{ V}$$

(8)

The graphs for the functions $kU_R$ and $U$ are shown in Figure 5.

![Fig. 5. Graphs for the functions kU and U - Block II](image)

The diagram of Block II is shown in Figure 6.

![Fig. 6. Diagram of Block II](image)

The circuit is an inverted amplifier-adder implemented with an operating amplifier (Rutkowski, 1975.)

LM385 is a source of reference voltage 2.5 V.

The three resistances $R_0$, $R_1$, $R_2$ are defined in the following way:

$$I_1 = \frac{U_R}{R_1}$$

(9)

$$I_2 = \frac{2.5}{R_2}$$

(10)

$$I_0 = I_1 - I_2$$

(11)

$$U = -R_0I_0 = -R_0(I_1 - I_2) = R_0I_2 - R_0I_1$$

(12)

From (5') $U = U_0 - kU_R$

When (12) and (5') are compared, the following expression is obtained:

$$U_0 = R_0I_2 = R_0 \frac{2.5}{R_2}$$

(13)

The value of $U_0$ is 14.2 V.

The value 20 k$\Omega$ is chosen for $R_0$. 


From (13) the value of $R_2$ is defined:

$$14.2 = 20 \cdot 10^3 \frac{2.5}{R_2} \Rightarrow R_2 = 3521 \Omega$$

$$kU_R = R_0j_l$$  \hspace{1cm} (14)

[follows from (12) and (5')]\]

$$kU_R = R_0 \frac{U_R}{R_1}$$, $U_R$ is cancelled

$$31.5 = 20 \cdot 10^3 \frac{1}{R_1} \Rightarrow R_1 = \frac{20 \cdot 10^3}{31.5} = 635 \Omega$$

**Third Stage - Block III**

Block III should implement the reverse function between the input value $U$ and the output value $E$. Thus, the straight function is $R_{\text{in}} \rightarrow U$ and the reverse one is $U \rightarrow E$, where there should be linear dependence between $R_{\text{in}}$ and $E$.

The voltage $U$ ($R_{\text{in}}$) enters at the input of Block III. The graph of this dependency is shown in Figure 5, the values of the argument (independent magnitude) $R_{\text{in}}$ are plotted to the x-axis and the values of the function $U$ are plotted to the y-axis.

We now take this characteristic experimentally by exchanging the places of the coordinate axes. The values of the argument $R_{\text{in}}$ are plotted to the y-axis at every 5 k$\Omega$, and the corresponding values of $U$ are plotted to the x-axis. In this operation, we get the reverse function of the $U(R_{\text{in}})$ function. The $R_{\text{in}}$ values are set using decade resistance box, and the respective values of $U$ are measured with an exact voltmeter at the outlet of Block II (Figure 6).

The graph is drawn on millimetre paper using 20 points and we try to approximate it with line segments. When the number of line segments is greater, the approximation is more accurate, but the circuit of Block III becomes too complicated.

Four line segments have been selected which are connected in three refraction points. This is done visually on the graph, trying to bring the line segment and the corresponding curve as close as possible.

Figure 7 shows the graph of the reverse function and its approximation through four line segments. The voltage $U$ is in the range of 1 V to 10 V and the refraction points are 6 V, 8 V and 9 V.

The angle factors in the equations of the straight lines are $K_0$, $K_1$, $K_2$ and $K_3$. These factors are defined by the graph and are respectively:

$$K_0 = \tan \alpha_0 = \frac{1}{3}; \hspace{0.5cm} \alpha_0 = 18.4^\circ$$

$$K_1 = \tan \alpha_1 = \frac{3}{4}; \hspace{0.5cm} \alpha_1 = 36.9^\circ$$

$$K_2 = \tan \alpha_2 = 2; \hspace{0.5cm} \alpha_2 = 63.4^\circ$$

$$K_3 = \tan \alpha_3 = 5; \hspace{0.5cm} \alpha_3 = 78.7^\circ$$

The angles of the slope $\alpha_0$, $\alpha_1$, $\alpha_2$ and $\alpha_3$ are between the respective line segments and the x-axis (Figure 7).

**Fig. 7. Graph of the approximated function $U(R_{\text{in}})$.**

In fact, Block III implements the reverse function approximated through four line segments. It represents a linear amplifier with a changing gain. (Sheingolf, 1974) The line diagram is shown in Figure 8.

**Fig. 8. Line diagram of Block III**

When changing $U$ from 1V to 6V, the gain is $K_0$ and the three diodes are turned off.

$$K_0 = \frac{R_f}{R_0}$$  \hspace{1cm} (15)

In the interval from 6 V to 8 V, diode $D_1$ is switched on and connects the resistance $R_1$ parallel to $R_0$. The gain increases $K_1 > K_{0\text{--}}$.

To define the values of the resistances $R_0$, $R_1$, $R_2$ and $R_3$ it is easier to work with the respective conductivities $g_0$, $g_1$, $g_2$ and $g_3$.

$$K_0 = \frac{1}{3}; \hspace{0.5cm} g_0 \approx R_f$$  \hspace{1cm} (15')
The value 10 K is accepted for $R_f$.

$$R_f = 10000 \text{ \Omega}$$

$$\frac{1}{3} = g_0 \cdot 10000 \quad g_0 = \frac{1}{30000} \text{ S}$$

$$R_o = 30 \text{ k}\Omega$$

$$K_1 = \frac{3}{4} \quad K_1 = (g_0 + g_1)R_f = K_o + g_1R_f$$

$$\frac{3}{4} = \frac{1}{3} + g_1 \cdot 10000$$

$$g_1 = \frac{3/4 - 1/3}{10000} = \frac{5}{120000} \text{ S}$$

$$R_1 = \frac{120000}{5} = 24000 \text{ \Omega}$$

$$r_1 = 24 \text{ k}\Omega$$

$$K_2 = 2 \quad K_2 = (g_0 + g_1 + g_2)R_f = K_1 + g_2R_f$$

$$2 = \frac{3}{4} + g_2 \cdot 10000$$

$$g_2 = \frac{2 - 3/4}{10000} = \frac{5}{40000} \text{ S}$$

$$R_2 = \frac{40000}{5} = 8000 \text{ \Omega}$$

$$R_2 = 8 \text{ k}\Omega$$

$$K_3 = 5 \quad K_3 = (g_0 + g_1 + g_2 + g_3)R_f = K_2 + g_3R_f$$

$$5 = 2 + g_3 \cdot 10000$$

$$g_3 = \frac{3}{10000} \text{ S}$$

$$R_3 = \frac{10000}{3} = 3333 \Omega$$

$$R_3 = 3.33 \text{ k}\Omega$$

Thus, the resistances which define the gain are:

$$R_f = 10 \text{ k}\Omega;$$

$$R_0 = 30 \text{ k}\Omega; \quad R_1 = 24 \text{ k}\Omega;$$

$$R_2 = 8 \text{ k}\Omega; \quad R_3 = 3.33 \text{ k}\Omega$$

The resistances which define the thresholds of switching on of the respective diodes are $R_A$, $R_B$ and $R_C$.

The diode $D_1$ is switched on when the potential of its anode is equal to zero as is the potential of the cathode. Shortly before $D_1$ is switched on, the current through $R_1$ and $R_o$ is equal to:

$$I_A = \frac{6}{R_1} = \frac{2.5}{R_A}, \quad R_A = \frac{2.5 \cdot 24000}{6} \text{ } \Omega$$

It is assumed that the three diodes are ideal. $R_o$ and $R_c$ are defined in the same way.

$$I_B = \frac{8}{R_2} = \frac{2.5}{R_B}, \quad R_B = \frac{2.5 \cdot 8}{3} \text{ } \Omega$$

$$I_C = \frac{9}{R_3} = \frac{2.5}{R_C}, \quad R_C = \frac{2.5 \cdot 3333}{9} \text{ } \Omega$$

Thus, the resistances which define the refraction thresholds are:

$$R_A = 10 \text{ k}\Omega$$

$$R_B = 2.5 \text{ k}\Omega$$

$$R_C = 926 \text{ \Omega}$$

What needs to be explained now is why it is necessary to have one more reference source 2.5 V for the resistance $R$.

Since the graph on Figure 7 does not start from zero, it is necessary to change the coordinate system which is shown on Figure 9.

Fig. 9. Transformation of the coordinate system.

In the coordinate system $x-y$ the function is:

$$y = K_0 \cdot x$$

In the new coordinate system $X-Y$

$$Y = K_0 \cdot (X - 1) + 1$$

where

$$K_0 = \frac{1}{3}, \quad x = X - 1$$

then

$$Y = \frac{1}{3} X + \frac{2}{3}$$

From the expression (24) it can be seen that it is necessary to lift the whole graph up along the $y$-axis with $2/3$ V. This is done with a reference source 2.5 V and resistance $R$. The $R$ value is defined in the following way:
Thus, all resistances from the Block III circuit are defined (Figure 8).

At the output of Block III a voltage divider is connected and a digital voltmeter realised with HC ICL7107 and a display of LED $3 \frac{1}{2}$ digits (Faulkenberry, 1982.)

When the resistance is equal to 20 kΩ, the display shows 19.9 kΩ, at 200 kΩ - 199.9 kΩ. The decimal point does not move.

**Defining the relative error**

To define the biggest relative error in a given interval, the function $U(R_{\text{ins}})$ is presented in the following way:

$$U = 14.2 - 31.5 \cdot \frac{1.6 \cdot R_{\text{ins}} + 220}{22 \cdot R_{\text{ins}} + 400}$$

(26)

And respectively:

$$R_{\text{ins}} = \frac{400U + 4400}{262 - 22U}$$

(27)

where $R_{\text{ins}}$ is in kΩ.

An interval $U (6 \div 8) \text{V}$, whose average is 7 V (Figure 10), is selected as an example.

![Graph for defining the relative error](image)

**Fig. 10. A graph for defining the relative error.**

We define the $R_{\text{ins}}$ values in three points – 6, 7 and 8 V.

$$R_a = \frac{400 \cdot 6 + 4400}{262 - 22 \cdot 6} = 52.3 \text{kΩ}$$

(28)

$$R_f = \frac{400 \cdot 7 + 4400}{262 - 22 \cdot 7} = 66.6 \text{kΩ}$$

(29)

$$R_a = \frac{400 \cdot 8 + 4400}{262 - 22 \cdot 8} = 8.4 \text{kΩ}$$

(30)

The exact value of $R_{\text{ins}}$ is designated with $R_f$ on Figure 10 and with $R_a$ – the measured value on the line segment for approximation.

In the case:

$$R_f = R_T = 66.6 \text{kΩ}$$

(31)

$R_a$ is equal to the mean value from $R_s$ and $R_a$

$$R_a = \frac{52.3 + 88.4}{2} = 70.3 \text{kΩ}$$

(32)

The biggest relative error in the interval used as an example is:

$$\delta \% = \frac{R_a - R_f}{R_f} \cdot 100 = \frac{70.3 - 66.6}{66.6} \cdot 100 = 5.5\%$$

(33)

To conclude, it should be noted that if we want to achieve the smallest error due to the approximation, we should not use four line segments but five, or more precisely six.

All calculated resistances can be regulated. The setting procedure is not described as it is too long and is related to the practical implementation of the converter.

**Conclusions**

The developed device for measuring the insulation resistance is fully compatible with the AZUR device. It is realised by means of an analogue converter, which linearises the non-linear characteristics current-resistance. The applied light indicator allows for more accurate and easier reading of the insulation resistance in the grid. The measuring range and the relative error meet the requirements for control of the insulation resistance in mine electrical grid with isolated star centre.

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