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AND PROCESSING OF RAW
MATERIALS
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Dear readers and authors,

It is a great honour for me to present to your attention the second 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 BASE included in OpenAIRE, the Russian Scientific Electronic Library (eLIBRARY) and the National Reference List of Contemporary Bulgarian Scientific Publications with Scientific Review achieved in COBISS.

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.

This volume of the journal is available due to the efforts of:

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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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ONLINE X-RAY FLUORESCENCE SCREENING OF ORE FOR SILVER AT THE MINES OPERATED BY KAZAKHMYS CORPORATION LLC

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ABSTRACT. This paper discusses the process and methodological aspects of X-ray fluorescence online monitoring of ore silver grade at the underground mines and open pits operated by Kazakhmys Corporation LLC. The analysis was complicated by the requirement to: a) ensure reliable silver grade determination of ore, starting at 1+ ppm; b) sample mine faces in vertical sections to a height of up to 7 m. For geophysical online monitoring of ore material in the walls of mine workings and in the broken rock mass, a portable energy-dispersive X-ray fluorescence spectrometer RPP-12T (Aspap Geo LLC, Alma-Ata) was developed, assembled, and comprehensively tested. The results of investigations carried out using the RPP-12T spectrometer are discussed. The data collected during the investigations made it possible to implement online ore silver grade monitoring in the underground mines and open pits operated by Kazakhmys Corporation LLC.

Key words: X-ray fluorescence method, energy-dispersive X-ray fluorescence spectrometer RPP-12T, online ore grade monitoring

Introduction

Kazakhmys Corporation LLC is a major copper company operating in Kazakhstan. Ore is mined at the Zhezkazgan, Balkhash, and Karaganda sites. Cuprous sandstone deposits Zhezkazgan, Zhaman-Ayat, Zhilanda Group (Itauz, Eastern Saryoba, Western Saryoba, Kipshakpay, Karashoshak), as well as complex copper-containing polymetallic deposits characterised by a wide grade range of valuable, associated, and impurity minerals are currently operated: the porphyry gold-copper Nurkazgan deposit, the pyrite-copper-lead-zinc Kusmuryn and Akbastau deposits, the gold-pyrite-copper-lead-zinc Abyz deposit, the Sayak group of copper-skarn deposits, the porphyry copper Konyrat deposit, and the porphyry copper-uranium Shatyrkol deposit (Satpayeva, 2005).

To efficiently conduct exploration and mining operations at such complex deposits, reliable means are required of online geophysical monitoring of the elemental composition and metal grade of the ore in in-situ rock, broken bulk rock mass, transportation vehicles, on process conveyer belts, and in exploration core samples.

In mining geophysical sampling, the emphasis is now placed not only on monitoring the grade of the primary (copper) mineral, but also on monitoring the grade of associated minerals (first of all, silver). Extraction of associated silver is a significant factor contributing to the economic performance of Kazakhmys Corporation LLC. Managing controlled extraction of associated silver and other associated ore minerals at the mining operations of Kazakhmys Corporation LLC is an urgent operational challenge. This study addresses this problem.

Factors complicating the implementation of effective online monitoring of ore silver grade are the following:

- Low silver grade ranging from 15 ppm in the ores of the Zhezkazgan, Zhaman-Albat, and Zhilanda cuprous sandstone deposits to 2–3 ppm at the Konyrat and Nurkazgan deposits;
- Horizontal and gently sloping ore bodies at the Zhezkazgan, Zhaman-Albat and Zhilanda deposits requiring sampling of mine faces and ledges in vertical sections up to 7 m high, which causes problems when delivering the instrument sensors to the required height and ensuring safety during geophysical sampling;
- Control system for associated silver mining will be effective only if the geophysical monitoring technology is able to reliably measure ore silver grades starting at 1+ ppm, which is the limit for the majority of online analysers, both laboratory and portable.

It is clear that ensuring reliable determination of ore silver grade by geophysical methods in the process of geophysical online monitoring of ores is a very complex task, both methodologically and technically. In addition, given the scale of production at Kazakhmys Corporation LLC operations, the technology vendor and its service centres must be located in Kazakhstan.

The study presented here addresses the above-mentioned problems.

Materials and methods

Since 1971, energy dispersive X-ray fluorescence (EDXRF) has been the primary method of geophysical ore sampling and analysis at Zhezkazgan. This method was chosen as the main research method.

In our geophysical investigations, we used portable EDXRF spectrometers RPP-12T, developed by Aspap Geo LLC (Almaty, Kazakhstan) specifically for measuring low grades of silver, cadmium, and a number of other elements, as well as for X-ray fluorescence sampling (XRF) of high faces (Dosmukhamedov, Lezin, 2011; Dosmukhamedov et al., 2012, Dosmukhamedov et al., 2013). A simplified mathematical model for calculating the abundances of elements in the EDXRF spectrometer RPP-12T is discussed in detail in (Yefimenko 2009).

The portable EDXRF spectrometers Spectroscан-GEO (SPECTRON, Ltd, St. Petersburg, Russia) and Elvax GEO (Elvatech, Ltd, Kyiv, Ukraine) were considered as an alternative (Moschevikin, Soloviev, 2020). But they did not fit in terms of weight parameters, the lack of the ability to raise the sensor to a height of 7 m and the considerable remoteness of firms from the mines of Kazakhmys Corporation LLC. For the same reasons, the use of EDXRF spectrometers of well-known world brands was not considered.

Two modifications of the RPP-12T EDXRF spectrometer were used in the studies: underground mine version (Figure 1A,
open-pit version (Figure 2A, 2B) and core version (Figure 1B). RPP-12T has a powder sample XRF function (Figure 3) for XRF of powder samples on the surface or XRF sampling of cuttings from holes drilled into the roof and bottom of mine workings directly in the underground mine.

The standard handheld spectrometer RPP-12T comes with two-meter rods (in this case, face XRF sampling height will be 4 m (Figure 2C.1). For Zhezkazgan, the number of rods was increased to 4–5 (Figure 2C.2). Sensor weight is 1.5 kg.

2B), open-pit version (Figure 2A, 2B) and core version (Figure 1B). RPP-12T has a powder sample XRF function (Figure 3) for XRF of powder samples on the surface or XRF sampling of cuttings from holes drilled into the roof and bottom of mine workings directly in the underground mine.

The standard handheld spectrometer RPP-12T comes with two-meter rods (in this case, face XRF sampling height will be 4 m (Figure 2C.1). For Zhezkazgan, the number of rods was increased to 4–5 (Figure 2C.2). Sensor weight is 1.5 kg.

Our know-how represents use of a mass-produced smartphone (Figure 1C and 2B) with an Android operating system and an impact-resistant body (protection class IP67) as the registration and processing unit. Competing solutions use pocket personal computers, whose capabilities are much lower. Wireless (via Bluetooth) data transmission from the sensor to the processing unit significantly increases the safety of the sampling process in high mine faces. RPP-12T supports mine face XRF sampling for 34 elements: Cu, Zn, Pb, Ag, Cd, As, Se, Ba, Fe, Mo, Mn, Ti, V, Cr, Co, K, Ca, Ni, Ga, Br, Rb, Sr, Zr, Y,
In, Pd, Nb, Sn, Sb, Te, Bi, W, Th, U. The field of view of the XRF sampling surface is 4–5 cm²; measurement exposure at one observation point is from 5 sec; detection limits for most ore elements range between n×10⁻⁴% and n×10⁻³%.

Solutions that make it possible to measure silver grade starting at 1+ ppm by using RPP-12T are as follows:

- high-speed silicon drift detector (SDD);
- small-sized X-ray emitter 50 kV, 10 W;
- optimised excitation of the analytical profiles of silver K-series;
- state-of-the-art high-performance electronics;
- reliable methodology and capable software.

The above device features made it possible to increase the luminosity (input load over 100 kHz) of the excitation and detection unit and the signal/background ratio and, thereby, significantly improve the sensitivity of the RPP-12T spectrometric channel to silver, which made it possible to confidently operate the spectrometer at silver grades from 1+ ppm with an XRF exposure at the observation point of 10 sec.

RPP-12T has a highly durable and protected design and does not require high operator's skills. The continuous operation time of RPP-12T on same battery set (in the 1st rod) is at least 10 hours.

To demonstrate the ability of the RPP-12T spectrometer to measure silver grades starting at 1+ ppm, an extensive testing and experimental programme was carried out (Yefimenko et al., 2014, Yefimenko et al., 2016). The main testing conditions are the following:

1. Core samples from exploration boreholes at the Zhezkazgan deposit were examined in Core Sample mode as follows: a) XRF measurements on 1 m core samples in boxes in a continuous mode with the sensor moving along the core sample at a rate of 20 sec/m, Figure 4B; b) XRF of 1 m core samples with a sampling increment of 10 cm (10 sampling points per m) and 20 cm (5 sampling points per m) with an exposure of 10 seconds and 5 seconds for each increment; c) verification XRF of 1 m core samples using the measurement modes specified in (a) and (b). Verification XRF in (b) had a slight shift.

2. XRF of the coarsely ground ore sample from a railway car (5–6 kg each) taken from two ore compositions (Kresto-7 open pit) at Zhezkazgan Concentrator 1. On each sample, 35–40 measurements were made with an exposure of 10 seconds (Figure 4A). Measurement mode was Naturally Occurring Ore.

3. XRF of reference ore specimens (of State Standard Ore Samples - SSOS) (Tsentgeolanalit, 2021) in Naturally Occurring Ore mode. Five measurements of 10 seconds each were taken across the sample in Naturally Occurring Ore mode.

4. XRF of exploration core sample by comparing the analysis results obtained with RPP-12T and an alternative portable EDXRF spectrometer Spectroscan Geo by NPO Spektron LLC (St. Petersburg, Russia). It should be emphasised that the XRF conditions were different: RPP-12T was used for core XRF in a continuous mode (Figure 4B); Spectroscan Geo was used for core XRF using a tripod (Figure 4C). We note that Spectroscan Geo is heavier (2.4 kg), has only two 1 meter long thin rods, and comes with a less powerful pocket personal computer (624 MHz vs. 2500 MHz).

5. High face XRF - at a height of 7 m.

6. XRF of powder ore sample using the Sample Analysis function. The measurement mode was Powder Sample. The measurement exposure time was 30 seconds.

7. XRF of Standard ore reference samples (SSOS –3029) - the measurement mode was Powder Sample and the measurement exposure 30 seconds. Sample Analysis option was used.

![A. Car sample](image1)
![B. RPP-12T core sample](image2)
![C. Spectroscan Geo core sample](image3)

**Fig. 4. Experimental work**

**Results and discussion**

The results from studies of ore samples from exploration boreholes at the Zhezkazgan deposit are presented in Table 1.

The data in Table 1 shows that the fit between the average silver grades in 1 m core sample intervals determined by XRF and chemical assay is fully compliant with the standards required by the mine geologists at Kazakhmys Corporation LLC operations (Yefimenko et al., 2016). The results of a study on off-grade copper intersections (not shown in Table 1) showed that RPP-12T is capable of reliable online monitoring of silver grade, starting at 1+ ppm.

The XRF results from measurements of the coarsely ground ore sample from a railway car taken from two ore compositions (Kresto-7 open pit) at Zhezkazgan Concentrator 1 were as follows: copper 3.03% and 2.28% (chemical assay 2.98% and 2.39%), silver 57.5 ppm and 37.7 ppm (chemical assay 52.5 ppm and 39.4 ppm), cadmium 4.1 ppm and 6.3 ppm (chemical assay 4.4 ppm and 5.9 ppm). The results confirm the good fit between the XRF data obtained by using RPP–12T and the chemical assays.
Table 2 shows an XRF report for the reference ore sample No 51 (Tsentgeolanalt, 2021) with a low silver grade (verified grades are Cu = 0.15%, Zn = 0.48%, Pb = 0%, Ag = 2.2 ppm, Cd = 37.0 ppm). As it can be seen, the RPP-12T is capable of reliably determining silver grades of 2.0 ppm.

The results from exploration of core sample by comparing the analysis results obtained with RPP-12T and the alternative portable EDXRF spectrometer Spectroscan Geo are presented in Table 3. Data on chemical assays are also shown in the table. As it can be seen from Table 3, the RPP-12T spectrometer performed very well giving data nearer to the chemical analyses figures.

Concerning the high face analysis, it was shown that the RPP-12T spectrometer is capable of carrying out XRF of mine faces to a height of 7 m. Figure 2C illustrates XRF at a height of 3 m and 6 m.

Table 1. RPP-12T Core sample XRF for silver, ppm

<table>
<thead>
<tr>
<th>Int. No</th>
<th>Continuous 10 points/m</th>
<th>5 s</th>
<th>5 points/m</th>
<th>Control 10 s</th>
<th>Primary 5 s</th>
<th>Control 5 s</th>
<th>Primary 5 s</th>
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<td>41</td>
<td>3.7</td>
<td>4.2</td>
<td>4.2</td>
<td>3.2</td>
<td>3.7</td>
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<td>4.9</td>
<td>5.6</td>
<td>4.5</td>
<td>3.8</td>
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<td>61</td>
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<td>8.2</td>
<td>7.8</td>
<td>7.0</td>
<td>6.6</td>
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<td>16.1</td>
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<td>15.8</td>
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<td>17.1</td>
<td>18.0</td>
<td>15.9</td>
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<td>56</td>
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<td>17.7</td>
<td>23.4</td>
<td>15.7</td>
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<td>23.0</td>
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<td>48</td>
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<td>43.1</td>
<td>40.4</td>
<td>45.0</td>
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</tr>
<tr>
<td>50</td>
<td>46.1</td>
<td>44.1</td>
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<td>44.6</td>
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<td>17.3</td>
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<td>Avg.</td>
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<td>18.2</td>
<td>18.8</td>
<td>17.3</td>
<td>17.1</td>
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<tr>
<td>σ</td>
<td>4.6</td>
<td>4.4</td>
<td>3.6</td>
<td>2.4</td>
<td>1.9</td>
<td>2.1</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Table 2. XRF of the reference ore sample No 51 (Tsentalganalt, 2021)

<table>
<thead>
<tr>
<th>No</th>
<th>Cu, %</th>
<th>Ag, ppm</th>
<th>Zn, %</th>
<th>Pb, %</th>
<th>Cd, ppm</th>
<th>Fe, %</th>
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<tbody>
<tr>
<td>1</td>
<td>0.13</td>
<td>2.3</td>
<td>0.51</td>
<td>0.00</td>
<td>38.7</td>
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<td>2</td>
<td>0.14</td>
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<td>0.00</td>
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<td>0.00</td>
<td>38.2</td>
<td>1.59</td>
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<td>2.4</td>
<td>0.48</td>
<td>0.00</td>
<td>38.2</td>
<td>1.52</td>
</tr>
<tr>
<td>5</td>
<td>0.14</td>
<td>2.1</td>
<td>0.50</td>
<td>0.00</td>
<td>35.0</td>
<td>1.47</td>
</tr>
<tr>
<td>Average</td>
<td>0.141</td>
<td>2.0</td>
<td>0.493</td>
<td>0.00</td>
<td>37.6</td>
<td>1.52</td>
</tr>
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</table>

Table 3. Simultaneous core studies using the EDXRF spectrometers RPP-12T and Spectroscan Geo

<table>
<thead>
<tr>
<th>No</th>
<th>Interval, m</th>
<th>Cu, %</th>
<th>Zn, %</th>
<th>Ag, ppm</th>
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<tr>
<td></td>
<td>from</td>
<td>to</td>
<td>Chemical assay</td>
<td>RPP</td>
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<td>131.3</td>
<td>132.4</td>
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</tr>
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<td>2</td>
<td>135.4</td>
<td>136.4</td>
<td>0.50</td>
<td>0.443</td>
</tr>
<tr>
<td>3</td>
<td>136.4</td>
<td>137.5</td>
<td>0.46</td>
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</tr>
<tr>
<td>4</td>
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<td>138.5</td>
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</tr>
<tr>
<td>5</td>
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<td>0.449</td>
</tr>
<tr>
<td>10</td>
<td>143.5</td>
<td>144.5</td>
<td>0.20</td>
<td>0.204</td>
</tr>
<tr>
<td>Average</td>
<td>0.431</td>
<td>0.434</td>
<td>0.443</td>
<td>0.004</td>
</tr>
</tbody>
</table>

The results from analyses of powder ore samples are presented in Table 4. A good fit between the average copper and silver grades found with the aid of XRF and chemical assay was shown.
Table 5 shows the results of the studies of standard ore reference samples (Tsengoleanolit, 2021) carried out by RPP-12T and chemical analysis. As it can be seen a good fit is obtained between the average silver and other mineral grades obtained by XRF and chemical analysis. The RPP-12T spectrometer on powder samples of ores ensures the accuracy of analysis for Ag, Cd, Cu, Zn, and Pb, which falls within the tolerances of “Norms of permissible discrepancies between the results of analyses of products of the copper industry and the lead-zinc industry for the content of basic elements” (ST RK 3126-2017).

Table 4. XRF of powder samples

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Analysis</th>
<th>Cu %</th>
<th>Pb %</th>
<th>Zn %</th>
<th>Ag* %</th>
<th>Cd* %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RPP-12T</td>
<td>0.537</td>
<td>0.0356</td>
<td>0.0112</td>
<td>8.6</td>
<td>6.9</td>
</tr>
<tr>
<td>2</td>
<td>Chemical</td>
<td>0.55</td>
<td>0.037</td>
<td>0.0112</td>
<td>9.3</td>
<td>n/a</td>
</tr>
<tr>
<td>3</td>
<td>RPP-12T</td>
<td>1.533</td>
<td>0.1019</td>
<td>0.0243</td>
<td>24.6</td>
<td>7.1</td>
</tr>
<tr>
<td>4</td>
<td>Chemical</td>
<td>1.55</td>
<td>0.103</td>
<td>0.0243</td>
<td>25.9</td>
<td>n/a</td>
</tr>
<tr>
<td>5</td>
<td>RPP-12T</td>
<td>3.149</td>
<td>1.8666</td>
<td>0.786</td>
<td>34.9</td>
<td>70.2</td>
</tr>
<tr>
<td>6</td>
<td>Chemical</td>
<td>3.16</td>
<td>1.90</td>
<td>0.80</td>
<td>35.0</td>
<td>71.0</td>
</tr>
<tr>
<td>7</td>
<td>RPP-12T</td>
<td>40.312</td>
<td>2.243</td>
<td>2.899</td>
<td>707.7</td>
<td>290.0</td>
</tr>
<tr>
<td>8</td>
<td>Chemical</td>
<td>40.40</td>
<td>2.25</td>
<td>2.899</td>
<td>707.7</td>
<td>290.0</td>
</tr>
</tbody>
</table>

Table 5. Results from studies on standard ore reference samples (Tsengoleanolit, 2021) by XRF and chemical analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analysis</th>
<th>Cu %</th>
<th>Pb %</th>
<th>Zn %</th>
<th>Ag* %</th>
<th>Cd* %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2887</td>
<td>RPP-12T</td>
<td>0.537</td>
<td>0.0356</td>
<td>0.0112</td>
<td>8.6</td>
<td>6.9</td>
</tr>
<tr>
<td>2888</td>
<td>Chemical</td>
<td>0.55</td>
<td>0.037</td>
<td>0.0112</td>
<td>9.3</td>
<td>n/a</td>
</tr>
<tr>
<td>2889</td>
<td>RPP-12T</td>
<td>1.533</td>
<td>0.1019</td>
<td>0.0243</td>
<td>24.6</td>
<td>7.1</td>
</tr>
<tr>
<td>2891</td>
<td>Chemical</td>
<td>1.55</td>
<td>0.103</td>
<td>0.0243</td>
<td>25.9</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Conclusion

In conclusions it can be said that the study successfully addressed an extremely challenging from theoretical, methodological, technical point of view, as well as urgent operational problem of implementing geophysical online monitoring of silver grade (starting at 1+ ppm) in the walls of mine faces and mine workings in order to manage planned silver production at the mines operated by Kazakhmys Corporation LLC. The results obtained by using the portable RPP-12T spectrometer and chemical assays show that RPP-12T ensures reliable silver grade determination of the ore (starting at 1+ ppm) while being able to sample mine faces in vertical sections to a height of up to 7 m.

The data collected during the studies made it possible to implement online ore silver grade monitoring in the underground mines and open pits operated by Kazakhmys Corporation LLC.

The results obtained by using the portable RPP-12T spectrometer and chemical assays show that RPP-12T ensures reliable silver grade determination of the ore (starting at 1+ ppm) while being able to sample mine faces in vertical sections to a height of up to 7 m.

The data collected during the studies made it possible to implement online ore silver grade monitoring in the underground mines and open pits operated by Kazakhmys Corporation LLC.

References


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ST RK 3126-2017, Norms of permissible discrepancies between the results of analyzes of products of the copper industry and the lead-zinc industry for the content of basic elements, https://online.zakon.kz/m/Document/?doc_id=39910757.

APPLICATION OF PHOTOGRAMMETRY FOR DETERMINATION OF VOLUMETRIC JOINT COUNT AS A MEASURE FOR IMPROVED ROCK QUALITY DESIGNATION (RQD) INDEX

Vancho Adjski, Zoran Panov, Risto Popovski, Radmila Karanakova Stefanovska

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ABSTRACT. Rock quality designation (RQD) index, provides a general indication of rock mass quality and is widely used in many rock mass classification systems. From the literature review, it is concluded that the RQD methodology has several limitations and one of them is highlighted in this paper with the help of stochastic analysis with Monte Carlo simulation. The purpose of this paper is to improve the results of the RQD index through volumetric joint count (Jv) from accessible surface areas or when drill cores are not available. In this paper, we introduce a low-cost photogrammetric method for rock slope reconstruction with scaled and oriented 3D point cloud, ideally suited for geomechanical analysis. As an outcome, the 3D point cloud is then used to detect the discontinuity sets and to, define their orientation, normal spacing and persistence. Results are then used to calculate the number of joints per m², which is then used as input in the empirical correlation between the RQD index and the Jv. The main advantage of the proposed methodology is that it is completely based on open-source software.

Key words: RQD index, volumetric joint count, photogrammetry, discontinuity sets

Introduction

The rock mass varies with the evolution of the geological environment, producing complex structures with two components: intact rock and discontinuities (Palmström, 2001). To obtain information about the joint properties of the rock mass it is necessary to perform visual observations in the field or on drill cores (if available). The methodology according to which the observations are made has a great impact on the quality of the data used in the calculations and evaluations. The presence of joints in the rock mass, divides it into blocks that contribute to the stability and the mechanical behaviour of the rock structure (Palmström, 2005).

RQD is a critical index that is based on core recovery procedure for quantifying the degree of rock mass jointing (Vavro et al., 2015). The assessment of RQD is a crucial aspect for mineral excavation and is widely used for evaluating the stabilities of the rock masses. However, the methodology of the traditional RQD can yield inaccurate assessments due to limitations within the methodology itself (Haftani et al., 2016; Pells et al., 2017; Chen et al., 2018; Chen and Yin 2019). These limitations can influence the results within the classification systems where the RQD is used, such as Rock Mass Rating (RMR) system, Q-system, and Oslope-system.

The volumetric joint count (Jv) measurements take into account all the joints in a three-dimensional rock mass and is a useful measure about the number of joints in a unit volume of rock masses (Palmström, 2001). The volumetric joint count can give much better characterisation for the degree of rock mass jointing.

The literature review point to the fact that the estimation of RQD with low value of error is crucial for engineering assessments. In this regard, several methods have been created to overcome the limitations inside the traditional RQD methodology, such as the weighted joint density (WJD) (Palmström, 1995, 1996). Modified WJD (Haftani et al., 2016), Volumetric joint count (Jv) (Palmström, 1982, 1985), Modified blockiness index (Bz) (Chen et al., 2019) and Improved Rock Quality Designation (RQD) (Azimian, 2016).

In the last years, the use of remote sensing techniques for rock mass characterisation has increased dramatically. Lidar scanning and digital photogrammetry techniques have been used to create 3D models for stability analysis and joint properties of the rock mass.

Buyer and Schubert (2017) proposed a method to identify discontinuity sets in a point cloud, generated from photogrammetry and calculate the spacing of the joint sets. Kim et al. (2013) presented photogrammetry based methodology to provide 3D models for estimation of the Joint Roughness Coefficient (JRC) values. Macciotta et al. (2020) used the photogrammetric techniques combined with discrete fracture network models to reliably estimate the rock fall block volumes. Francioni and coauthors (2019) proposed a new method of using photogrammetry for creation of scaled and georeferenced 3D models from rock slopes. The obtained 3D models from the proposed approach have been validated against a laser scanning point cloud and the advantages and limitations of the proposed method are highlighted.

Recent literature review and the rapid development in the field of digital photographing and development of 3D point clouds, encouraged the authors to present methodology for determination of volumetric joint count through photogrammetry. In the development process of the presented methodology the authors used open-source software. The focus of this study is the implementation of free open-source software to analyse the results obtained from the point cloud data for the purpose of improving the results of the RQD index through volumetric joint count. The procedure that was followed in this study is shown in Figure 1.

Methods

Limitations of traditional RQD methodology

The RQD was first introduced in 1963 by Deere to provide a quantitative estimate of rock mass quality from drill core logs. RQD is defined as the percentage of the total length of core pieces longer than 10 cm (L) to the total length of the core run (L):

$$RQD = \frac{\sum L_i}{L} \times 100 \%$$  (1)

Several limitations in the RQD methodology emerged from a substantial bibliographical review, expressed as follows (Haftani et al., 2016; Pells et al., 2017; Chen et al., 2018; Chen, Yin 2019):
For example, RQD = 0 % where the distance between the joints in the drill cores is 9 cm or less, while RQD = 100 % where the distance between the joints is 11 cm or more, see Figure 2a).

The traditional RQD methodology does not give any information about the quality of core pieces smaller than 10 cm in length.

The RQD value is anisotropic and sensitive to the orientation of joint sets and dependent on the direction of the borehole (Figure 2b).

By emphasizing the limitations in the RQD methodology, the calculations made need to be used with caution because they may often lead to inaccuracy or errors. Literature review from several authors point out that in practice the RQD methodology values tend to be either high or low (often above 70% or below 10 to 20 %) in most rock engineering projects (Harrison 1999; Hack 2002). This statement was tested by the authors using a Monte Carlo simulation (Adjiski et al., 2019). Figure 3 shows the model used for the Monte Carlo simulation.

Table 1 shows the RQD (%) results from the Monte Carlo simulation models for each of the generated fracture frequency in 100 cm drill core length. For the purpose of this paper, 10 000 simulations were performed for each of the generated fracture frequency and the results were grouped into RQD values from 0 to 100 (%) with 10% increments.

Figure 4 shows the graphical display in the form of a histogram, in which all RQD (%) values of the Monte Carlo simulation models are grouped into percentage frequency ranges. The results show that more data are in the range above 75 % or below 25 % which is close to the statement from several authors about the tendency of the RQD values to be either high or low in most rock engineering projects.
Fig. 3. Monte Carlo simulation models for the generation of uncertainty in fracture frequency parameters of drill core to evaluate the RQD index

Table 1. Results from the Monte Carlo simulation models

<table>
<thead>
<tr>
<th>Fracture frequency</th>
<th>RQD (%)</th>
<th>0-10</th>
<th>11-20</th>
<th>21-30</th>
<th>31-40</th>
<th>41-50</th>
<th>51-60</th>
<th>61-70</th>
<th>71-80</th>
<th>81-90</th>
<th>91-100</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N⁰</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fracture frequency=2</td>
<td>N⁰</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>10000</td>
</tr>
<tr>
<td>Fracture frequency=4</td>
<td>N⁰</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>511</td>
<td>9486</td>
</tr>
<tr>
<td>Fracture frequency=6</td>
<td>N⁰</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>339</td>
<td>3287</td>
<td>6370</td>
</tr>
<tr>
<td>Fracture frequency=8</td>
<td>N⁰</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0.22</td>
<td>3.91</td>
<td>24.21</td>
<td>49.53</td>
<td>22.13</td>
</tr>
<tr>
<td>Fracture frequency=10</td>
<td>N⁰</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.02</td>
<td>0.87</td>
<td>6.45</td>
<td>24.21</td>
<td>40.91</td>
<td>24.06</td>
<td>34.8</td>
</tr>
<tr>
<td>Fracture frequency=12</td>
<td>N⁰</td>
<td>0</td>
<td>0.01</td>
<td>0.06</td>
<td>0.64</td>
<td>3.36</td>
<td>11.51</td>
<td>25.25</td>
<td>33.24</td>
<td>20.72</td>
<td>49.3</td>
</tr>
<tr>
<td>Fracture frequency=14</td>
<td>N⁰</td>
<td>0</td>
<td>0.71</td>
<td>2.15</td>
<td>7.38</td>
<td>18.65</td>
<td>25.95</td>
<td>24.58</td>
<td>15.29</td>
<td>4.81</td>
<td>0.47</td>
</tr>
<tr>
<td>Fracture frequency=16</td>
<td>N⁰</td>
<td>0.911</td>
<td>10.66</td>
<td>20.14</td>
<td>26.05</td>
<td>20.36</td>
<td>9.48</td>
<td>3.57</td>
<td>0.6</td>
<td>0.03</td>
<td>0</td>
</tr>
<tr>
<td>Fracture frequency=18</td>
<td>N⁰</td>
<td>3.411</td>
<td>18.10</td>
<td>20.46</td>
<td>16.65</td>
<td>7.7</td>
<td>2.42</td>
<td>0.52</td>
<td>0.04</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fracture frequency=20</td>
<td>N⁰</td>
<td>6.504</td>
<td>15.6</td>
<td>10.96</td>
<td>6.23</td>
<td>1.84</td>
<td>0.33</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Volumetric joint count

Palmström (1982, 1985) described the volumetric joint count ($J_v$) as a useful measure of the degree of joints intersecting a volume of rock mass. Volumetric joint count is a 3D measurement for the density of all the joints and it can be measured from the joint set spacings within a volume of rock mass as (Palmström, 2001):

$$J_v = \frac{1}{S_1} + \frac{1}{S_2} + \frac{1}{S_3} + \ldots$$

(2)

where, $S_1$, $S_2$, $S_3$ are the average spacings for the joint sets. In his research Palmström (2001) also mentioned that random joints could be included by using the following expression:

$$J_v = \frac{1}{S_1} + \frac{1}{S_2} + \frac{1}{S_3} + \ldots + \frac{N_r}{S_r}$$

(3)

where $N_r$ is the number of random joints and for the random joints spacing the experience indicates that this can be set to $S_r = 5$ m.

Palmström (1982) in his research suggested that, when drill cores are not available but surface exposures or exploration adits with discontinuity traces are visible and accessible, the RQD index can be estimated from the number of discontinuities per unit volume. The suggested relationship can be estimated by using the following expression:

$$RQD = 110 - 2.5J_v$$

(4)

($RQD = 0$ for $J_v > 44$, and $RQD = 100$ for $J_v < 4$)

Given the foregoing it can be concluded that RQD is a directionally dependent parameter closely related with the borehole orientation and the use of the volumetric joint count can significantly reduce this directional dependence.

Structure from motion photogrammetry

Structure from motion (SfM) is a photogrammetric technique which utilises a series of 2D overlapping images to reconstruct 3D surface models (Francioni et al., 2019). SfM technique can be used to create point cloud based 3D models of objects with consumer grade digital cameras. The advances in this photogrammetric technique, together with the advances of computers, digital cameras and unmanned aerial systems (UAS) have now made it feasible to be able to generate 3D models without expensive equipment.

In this research we propose a SfM photogrammetric technique to create a high resolution 3D rock slope model. The studied slope with a length of around 25 m and height of up to 15 m was selected for this study and is located in an open pit mine in N. Macedonia.

For the purpose of this model a total of 281 images were acquired to cover the rock slope with overlapping images. The images were captured using a Canon 450D camera with 50 mm focal length.

The overlapped images from the survey were processed using the open-source software Meshroom (2020), which resulted in a model that contains a dense point cloud with 7 105 230 points.

The process of georeferencing the model will be the subject of another study, since this model will represent a case for testing purposes. The proposed SfM methodology generates...
point clouds without scale or orientation, i.e. arbitrary reference system. However, to obtain discontinuity characteristics (orientation, spacing, persistence) from this model, it is still necessary to have an object of known geometry as a reference scale and orientation (García-Luna et al., 2019).

This methodology involves the use of ground control points (GCPs) for scaling, located on the slope and providing a reference during the creation of the 3D model (Figure 5a).

The GCPs utilised in this research is an Ethylene Vinyl Acetate (EVA) foam square with targets at the four corners and in the middle (Figure 5b). To correctly orient the generated 3D point cloud with SfM the three EVA templates have been positioned on the slope to provide the necessary reference and a geological compass is used to measure the dip and dip direction of the EVA template and also the inclination of the base of the EVA template. An important note to keep in mind is that the EVA templates must be located and oriented within the research scene before any photograph is taken. The next step is to use the open-source software CloudCompare (2020) to scale and orient the point cloud in relation with the EVA templates. The presented methodology is shown in Figure 6 where we highlighted the necessary steps of this procedure.

Fig. 5. a) Point cloud 3D model generated with Meshroom and marked position for GCPs b) EVA template used for GCPs

Fig. 6. Flowchart of the SfM methodology for creating properly scaled and oriented point cloud from the rock slope
Identification and analysis of discontinuity sets with DSE software

One of the most important parameters in rock engineering is to have knowledge about the discontinuity network within a rock mass. This information is of crucial importance to locate the discontinuities, bedding planes and joints which influence the behaviour and mechanical properties of rock masses.

For this purpose, the DSE (available on GitHub.com) an open-source software is introduced to identify the different discontinuity sets in a rock face from previously developed 3D point cloud (Riquelme et al., 2014; Papathanassiou et al., 2020).

This software analyses each single point within an unorganised 3D point cloud, searching its knn (k-nearest neighbours algorithm) and calculating the best fit plane of this subset.

The methodology behind the software is shown in Figure 7.

This process needs extensive computer power and because of this, a small area from the point cloud is selected. The selected part for the DSE analysis that has an area of 8.5×8.5 m and contains a point cloud with 1 113 250 points is shown on Figure 8.

Fig. 7. Step by step methodology for application of DSE open-source software

Fig. 8. Selected area for DSE analysis from the point cloud
Results and discussion

In order to estimate the volumetric joint count and use its value for empirical correlation with the RQD index, the generated point cloud was analysed by applying the previously mentioned methodology (Figure 1).

A point cloud is constructed with the open-source software Meshroom from the overlapping photos taken from the rock slope. The point cloud was then scaled and oriented with specially developed EVA templates with known dimensions and was used as GCPs (Figure 5 and 6).

In order to detect the discontinuity sets from the point cloud the studied area was analysed by the open-source software DSE. For this purpose, supervised classification of discontinuity sets was performed in the DSE software applying the methodology shown in Figure 7.

The method behind the DSE software is to assign a set to every point from the point cloud if the angle between the principal plane and the points normal is less than a specified threshold value. The parameters used in the DSE are as follows:

- number of nearest neighbours (knn) = 30;
- tolerance = 0.2;
- number of bins = 64;
- minimum angle that two poles can present = 300;
- maximum number of principal planes = 10;
- minimum angle between the normal vector of a discontinuity set and the normal vector of the point (cone) = 30.

Once the sets with the points members are extracted, for every cluster of points which is a member of a plane the software calculates the planes’ equations for every surface. This result is then used for calculation of the normal spacing and the persistence inside the DSE software.

As a result, four main discontinuity sets have been semi-automatically extracted and identified with the DSE software. Figure 9a shows the point cloud with single points symbolised by the different colours according to their assigned discontinuity set (from 1 to 4). Figure 9b) shows a lower-hemisphere stereographic projection of the density of the normal vectors poles and its corresponding principal poles based on DSE software.

The results presented in Table 2 show the mean dip direction and dip angles for each discontinuity set and their characteristics.

<table>
<thead>
<tr>
<th>Discontinuity set ID</th>
<th>Dip direction</th>
<th>Dip</th>
<th>Density</th>
<th>Number of assigned points to a discontinuity set over the total number of points (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Joint set 1</td>
<td>290.53</td>
<td>31.25</td>
<td>11.57</td>
<td>40.16</td>
</tr>
<tr>
<td>Joint set 2</td>
<td>26.58</td>
<td>29.75</td>
<td>2.27</td>
<td>18.51</td>
</tr>
<tr>
<td>Joint set 3</td>
<td>351.34</td>
<td>50.84</td>
<td>1.73</td>
<td>17.62</td>
</tr>
<tr>
<td>Joint set 4</td>
<td>307.02</td>
<td>64.10</td>
<td>0.79</td>
<td>12.77</td>
</tr>
</tbody>
</table>

Fig. 9. a) Point cloud where each point is coloured by their specific discontinuity set b) Stereographic projection of the normal vector density plot and its corresponding principal poles

Table 2. Discontinuity sets main properties obtained with DSE from the 3D point cloud

Taking into account the correlation between RQD and the volumetric joint count \( J_v \) proposed in Equation (5) by Palmström (2005), the RQD index when drill cores are not available is calculated as follows:

\[
RQD = 110 - 2.5 \times 18.57 = 63\% \tag{7}
\]

RQD index of the analysed rock mass in this paper is computed as 63% and this value according to Deere (1963) belongs to the “fair” classification (Figure 2c).
Conclusion

This study primarily aims to improve the results of the RQD index through volumetric joint count (Jv) when drill cores are not available or surface areas are visible and accessible. This work has also demonstrated that through the use of the proposed methodology, some of the limitations inside the traditional RQD index methodology will be avoided.

Using SfM methods and the availability of new high-resolution digital cameras and open-source software has led to a noticeable increase in the quality of engineering data that can be collected.

This research proposes a SfM photogrammetry method with the open-source software Meshroom for creation of a 3D point cloud of a rock slope located in an open pit mine in N. Macedonia. The method is based on the use of EVA templates of known geometry and orientation, located on the rock slope during the survey (Figure 5a, b). The EVA templates are used as GCPs which are then used to scale and orient the 3D point cloud with free CAD software of choice and the open-source software CloudCompare (Figure 6).

The oriented and scaled 3D point cloud obtained with the SfM methodology is then used for structural mapping of discontinuities with the open-source software DSE (Figure 7).

The DSE software gave good results for four main discontinuity sets and their mean orientations (Table 2). Additionally, the 3D point cloud was classified which allowed to perform additional calculations that include the normal spacing and the maximum persistence (Figure 10). The results are then used for calculation of the volumetric joint count (number of joints per m³).

The geo-mechanical quantitative estimate of the rock mass is then performed with the empirical correlation proposed by Palmström (2005), between the RQD index and the volumetric joint count (Jv).

The proposed methodology has several advantages which include the following:
- equipment needed is relatively inexpensive;
- no need for advanced photographic skills for the SfM photogrammetry methodology;
- no need for expensive tools for scaling and orientation of the 3D point cloud;
- the used software in the presented methodology is under the open-source licenses (free).

References


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SOLVENT EXTRACTION OF ZINC FROM ACIDIC LEACH SOLUTIONS

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ABSTRACT. An initial test work was carried out to demonstrate that solution produced by autoclave acid leaching of Electric Arc Furnace Dust (EAFD) from the steel production could be processed through solvent extraction (SX) to recover zinc. Solvent extraction is a process for purification of the leach solution that extracts mainly zinc from other metallic impurities. To assess zinc extraction different counter-current extraction and strip configurations were tested. Extractant D2-ethylhexyl phosphoric acid (D2EHPA) and ShellSol D100 as a diluent were used in this investigation. The main operational parameters and the results obtained in the test work are presented in this paper. Well over 90% of the zinc was extracted from the pregnant leach solution using multi-stage SX circuit configuration and pH adjustment. Details of circuit configurations, phase disengagement times and crud generation are also shown.

Key words: zinc, solvent extraction, circuit configuration

Introduction

Solvent extraction (SX) is a hydrometallurgical process used for the concentration and purification of the major metals such as uranium, copper, nickel and cobalt, but also for rare metals, e.g. tungsten, rare earths, thorium, vanadium, etc. (Kumar et al., 2011; Regel-Rosocka, Alguacil, 2013; Chauhan, Patel, 2014; Xie et al., 2014; Sole, Tinkler, 2016). Technically viable solvent extraction routes also exist for zinc and it is recovered in significant quantities by the process. D2-ethylhexyl phosphoric acid (D2EHPA) is the most widely used extractant in the industrial practice for zinc recovery from sulphate solutions.

This extractant is selective for zinc over copper, cadmium, cobalt, nickel, etc. and is easily stripped by sulphuric acid solutions like spent electrolyte from the electrowinning (EW) process (Cole, Sole, 2002). Extraction and stripping of zinc with D2EHPA can be represented by the following reaction (Martin et al., 2002):

\[ \text{Zn}^{2+} + 2(R-H)_{\text{org}} \leftrightarrow 2H^+ + (ZnR_2)_{\text{org}} \]

where: 
(R–H) is the D2EHPA reagent
(ZnR2) is the zinc-organic complex

In general, zinc SX circuit consists of the following main process steps, outlined in more details below:

- Extraction (E) - zinc containing Pregnant Leach Solution (PLS) is thoroughly mixed with an organic mixture and the zinc is selectively transferred from the aqueous to the organic phase. The organic mixture is composed of an organic reagent, called the extractant, dissolved in an essentially water-immiscible liquid hydrocarbon solvent, called the diluent.
- Washing - the zinc loaded organic phase is mixed with demineralised water to remove physically entrained halides.
- Scrubbing - the loaded organic is mixed with acidic zinc containing solution, typically diluted spent zinc electrolyte to remove co-extracted impurities from the loaded organic phase. This process step minimises the build-up of detrimental to the EW process impurities such as calcium, cadmium, copper, cobalt, nickel, etc.
- Stripping - the washed/scrubbed organic phase is contacted with an acidic aqueous solution, typically spent electrolyte from EW section and the zinc is transferred from the organic into the aqueous phase.
- Organic reagents regeneration - although selective for zinc over other metal cations, iron (III) is strongly extracted by D2EHPA. To remove iron (III) from the organic phase a bleed stream, typically 2-3% of total organic flow in the circuit, is regenerated with 6 M HCl in the this step (Musadaidzwa, Tshiningayamwe, 2009).

The SX circuit configuration is dependent on a number of variables, including the feed solution chemistry (zinc tenor, impurities and pH), strip electrolyte zinc and acid concentration, economics and operating philosophy of the plant (Soderstrom, Bednarski, 2007).

SX circuit configurations used in the industrial practice are as follows (MacKenzie, 1997):

- 2 extraction stages and 1 stripping stage (2E X 1S)
- 2 extraction stages and 2 stripping stages (2E X 2S)
- 3 extraction stages and 1 stripping stage (3E X 1S)
- 3 extraction stages and 2 stripping stages (3E X 2S)
- All of the above with additional parallel extraction (P) stage and/or washing/ scrubbing (W/Sc) stages.

Materials and methods

Pregnant Leach Solution (PLS) and Organic Phase

The zinc SX tests were carried out using zinc containing pregnant leach solution (PLS) obtained from laboratory scale autoclave acid leaching of Electric Arc Furnace Dust (EAFD), containing 22.7 % Zn. In the leach study, it was found that the material responds favourably to the process with zinc extraction of around 80%.

The optimal conditions in the leach stage were 10% solids, 65 g/l sulphuric acid, 110 °C temperature, 8 bar oxygen overpressure and 2 h leach time. The PLS (zinc SX feed) composition is shown in Table 1. The iron was removed from the zinc SX feed by precipitation using oxidation and neutralisation methods.

Solvent extraction tests were conducted with the organic phase composed of the extractant di-2-ethylhexyl phosphoric acid (D2EHPA) and the diluent ShellSol D100, both available commercially and used in various SX operations worldwide. Details of the extractant and the diluent used are given in Table 2 and Table 3 (Balesini Aghdam et al., 2011; Liu et al., 2021).
Table 1. PLS composition

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td>4.5</td>
</tr>
<tr>
<td>Na</td>
<td>ppm</td>
<td>200.5</td>
</tr>
<tr>
<td>Mg</td>
<td>ppm</td>
<td>653.2</td>
</tr>
<tr>
<td>Ca</td>
<td>ppm</td>
<td>820.8</td>
</tr>
<tr>
<td>Fe</td>
<td>ppm</td>
<td>0.142</td>
</tr>
<tr>
<td>Cu</td>
<td>ppm</td>
<td>133.6</td>
</tr>
<tr>
<td>Zn</td>
<td>ppm</td>
<td>18500</td>
</tr>
<tr>
<td>Al</td>
<td>ppm</td>
<td>368.4</td>
</tr>
<tr>
<td>Cd</td>
<td>ppm</td>
<td>40.23</td>
</tr>
<tr>
<td>Mn</td>
<td>ppm</td>
<td>968.3</td>
</tr>
<tr>
<td>Co</td>
<td>ppm</td>
<td>0.290</td>
</tr>
<tr>
<td>Ni</td>
<td>ppm</td>
<td>9.923</td>
</tr>
<tr>
<td>Pb</td>
<td>ppm</td>
<td>0.186</td>
</tr>
<tr>
<td>Cr</td>
<td>ppm</td>
<td>0.094</td>
</tr>
<tr>
<td>As</td>
<td>ppm</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Si</td>
<td>ppm</td>
<td>33.48</td>
</tr>
<tr>
<td>Sb</td>
<td>ppm</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Cl</td>
<td>ppm</td>
<td>0.110</td>
</tr>
<tr>
<td>TSS</td>
<td>ppm</td>
<td>32</td>
</tr>
</tbody>
</table>

Table 2. SX extractant characteristics

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product name</td>
<td></td>
<td>D2EHPA</td>
</tr>
<tr>
<td>Appearance</td>
<td></td>
<td>Clear liquid</td>
</tr>
<tr>
<td>Colour</td>
<td></td>
<td>Colourless or pale yellow</td>
</tr>
<tr>
<td>Flash point</td>
<td>°C</td>
<td>150</td>
</tr>
<tr>
<td>Bis(2-ethylhexyl) hydrogen phosphate content</td>
<td>%</td>
<td>95-99</td>
</tr>
<tr>
<td>Density @20°C</td>
<td>kg/m³</td>
<td>960-990</td>
</tr>
<tr>
<td>Viscosity @40°C</td>
<td>cP</td>
<td>21</td>
</tr>
</tbody>
</table>

Table 3. SX diluent characteristics

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product name</td>
<td></td>
<td>ShellSol D100</td>
</tr>
<tr>
<td>Type</td>
<td></td>
<td>High flash, slow evaporating hydrocarbon solvent</td>
</tr>
<tr>
<td>Appearance</td>
<td></td>
<td>Liquid</td>
</tr>
<tr>
<td>Colour</td>
<td></td>
<td>Colourless</td>
</tr>
<tr>
<td>Flash point</td>
<td>°C</td>
<td>105</td>
</tr>
<tr>
<td>Density @15°C</td>
<td>kg/m³</td>
<td>797</td>
</tr>
<tr>
<td>Viscosity @25°C</td>
<td>mm²/s</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Equipment

Batch solvent extraction tests were performed in a laboratory scale apparatus, as given in Figure 1. The apparatus consists of a 2 l glass vessel equipped with a removable stainless steel baffles (left) and a six-bladed impeller (right).

Analytical Methods

All aqueous samples were analysed for the various metal concentrations by Inductively Coupled Plasma Atomic Optical Emission Spectroscopy (ICP-OES).

Results and discussion

Single Stage Extraction

To assess zinc extraction efficiency from PLS, a single stage contact was carried out by contacting the aqueous solution and organic phase with an O/A ratio of 1.5:1 for 10 minutes. The results of the experiment are shown in Table 5:

Table 5. Single Stage Extraction Results

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn concentration in PLS</td>
<td>ppm</td>
<td>18500</td>
</tr>
<tr>
<td>pH PLS</td>
<td></td>
<td>4.5</td>
</tr>
<tr>
<td>Zn concentration in raffinate</td>
<td>ppm</td>
<td>8190</td>
</tr>
<tr>
<td>pH raffinate</td>
<td></td>
<td>0.93</td>
</tr>
<tr>
<td>Zn extraction</td>
<td>%</td>
<td>55.7</td>
</tr>
</tbody>
</table>
As can be seen, 55.7% of the zinc in the pregnant leach solution was extracted by the organic phase containing 40 vol.% D2EHPA in a single contact at pH value of 4.5.

Multiple Stage Extraction and Strip

For the multiple stage extraction and strip tests, 3EX2S circuit configuration was selected due to high zinc tenor in the PLS and high zinc recovery required. The circuit configuration comprises 3 extraction stages (E) and 2 stripping stages (S) as shown in Figure 2:

![Fig. 2. 3EX2S circuit configuration](image)

(PLS - Pregnant Leach Solution, LE - lean electrolyte, SE - strong electrolyte, l.o. - loaded organic, s.o. - stripped organic, E1 - first extraction stage, E2 - second extraction stage, E3 - third extraction stage, S1 - first stripping stage, S2 - second stripping stage)

Three series of multi-stage counter-current extraction and strip tests using 3EX2S circuit configuration were conducted with the main objective to achieve a zinc extraction efficiency of over 90%. The main control mechanism in the tests was the adjustment of the pH profile in the extraction stages. No pH adjustment was made in the first series, while in the other two pH was raised in E2, and E2 and E3 to ensure low levels of zinc in the raffinate. In the extraction PLS and organic phase were contacted in the test apparatus under test conditions, as given in Table 4. The pH was adjusted in the last extraction stages (E2 and E3) to around 2.5 by the addition of NaOH solution. This pH value, proposed by Pereira et al. (2007) was selected for the tests to ensure high zinc transfer and to minimise the impurities co-extraction. Samples of the PLS, aqueous effluents from E1, E2 and raffinate (E3), were taken at the end of each test and assayed for zinc to allow extraction efficiencies to be determined. The loaded organic phase was stripped in two counter-current stages S1 and S2 using sulphuric acid solution (180 g/l). Table 6, Table 7, Table 8 and Figure 3 show typical extraction efficiencies achieved during the tests.

![Table 6. 3EX2S circuit configuration test results, no pH adjustment (Test Series 1)](image)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn concentration in PLS</td>
<td>Ppm</td>
<td>18500</td>
</tr>
<tr>
<td>pH PLS</td>
<td></td>
<td>4.5</td>
</tr>
<tr>
<td>Zn concentration in raffinate</td>
<td>ppm</td>
<td>4350</td>
</tr>
<tr>
<td>pH raffinate</td>
<td></td>
<td>0.78</td>
</tr>
<tr>
<td>Overall Zn extraction</td>
<td>%</td>
<td>76.5</td>
</tr>
</tbody>
</table>

The following conclusions could be made from the results of the three test series:

- The highest overall zinc extraction efficiency of 98.2% was achieved at 3EX2S circuit configuration with pH adjustment in the extraction stages E2 and E3;

![Table 7. 3EX2S circuit configuration test results, pH adjustment in the extraction stage E2 (Test Series 2)](image)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn concentration in PLS</td>
<td>ppm</td>
<td>18500</td>
</tr>
<tr>
<td>pH PLS</td>
<td></td>
<td>4.5</td>
</tr>
<tr>
<td>Zn concentration in raffinate</td>
<td>ppm</td>
<td>1055</td>
</tr>
<tr>
<td>pH raffinate</td>
<td></td>
<td>1.21</td>
</tr>
<tr>
<td>Overall Zn extraction</td>
<td>%</td>
<td>94.3</td>
</tr>
</tbody>
</table>

![Table 8. 3EX2S circuit configuration test results, pH adjustment in the extraction stages E2 and E3 (Test Series 3)](image)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn concentration in PLS</td>
<td>ppm</td>
<td>18500</td>
</tr>
<tr>
<td>pH PLS</td>
<td></td>
<td>4.5</td>
</tr>
<tr>
<td>Zn concentration in raffinate</td>
<td>ppm</td>
<td>330</td>
</tr>
<tr>
<td>pH raffinate</td>
<td></td>
<td>1.64</td>
</tr>
<tr>
<td>Overall Zn extraction</td>
<td>%</td>
<td>98.2</td>
</tr>
</tbody>
</table>

- Optimisation of the pH in the extraction stages is requisite for the achievement of low levels of zinc in the raffinate and for high extraction efficiency.
- Key data and results from the solvent extraction test work are discussed in details below:
  - The preliminary SX test work consisted of small-scale tests with pregnant leach solution (PLS) produced in the leaching of electric arc furnace dust (EAFD) to determine the zinc recoveries, phase disengagement times and eventually - crud generation.
  - The analysis of the PLS (zinc SX Feed) indicates that impurity elements such as Ca, Mg, Mn, Fe, Cu and Cd would be co-extracted along with the Zn into the organic phase.
  - Solvent extraction tests were conducted with the organic extractant DEHPA dissolved in ShellSol D100. The extractant used was selected considering its availability, high selectivity for zinc over Cu, Cd, Co, Ni, and the halides and effectiveness for zinc recovery from a sulphate media essentially free of ferric iron (Deep, De Carvalho, 2008).
  - High DEHPA concentration of 40 v/v % in the organic phase was selected in order to ensure maximum zinc transfer in the tests.
• Approximately 56% of the zinc in the pregnant leach solution was extracted in a single stage extraction contact at pH value in the aqueous phase of 4.5.
• Approximately 76% of the zinc in the pregnant leach solution was extracted using 3EX2S circuit configuration, without pH adjustment in the extraction stages.
• The pH value in the extraction stages played a key role in achieving high zinc recoveries. pH adjustment of PLS to around 2.5 in 3EX2S circuit configuration by addition of NaOH solution gives zinc recoveries in the range of 94% - 98%.
• The extraction and stripping phase disengagement times were in the range of 60 – 90 seconds which is considered as normal.
• Phase separations were clear in all stages and no crud formation was observed.
• Further concentration and purification of the strip solution that is not however within the scope of this study, could produce an advance electrolyte, suitable for zinc electrowinning.

Conclusions

This paper presents initial experimental test work results for the recovery of zinc by solvent extraction using DEHPA as extractant from pregnant leach solution generated from leaching of electric arc furnace dust with Zn content of 18500 ppm.

The optimised 3EX2S circuit with pH adjustment in the extraction stages achieved zinc extraction and stripping efficiencies in the range of 94.3% – 98.2%.

Despite the promising results, obtained in this study, further, more detailed research work is required to optimise the organic phase composition and operating conditions, and to investigate the removal of co-extracted impurities with inclusion of washing/scrubbing stages in the SX circuit configuration.

References


MacKenzie M. 1997. The solvent extraction of some major metals – an overview, Henkel Australia Pty Ltd.


DEEP NEURAL NETWORKS APPLICATIONS IN THE STUDY OF A GEOLOGICAL INDICATOR

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ABSTRACT. The differences between shallow neural networks and deep neural networks are considered. Data from operational exploration of an open pit mine are used to train different types of deep neural networks to predict a useful indicator. The results of deep network training are compared both with each other and with previous results obtained from the training of shallow neural networks. The errors in training and testing of the models according to the number of layers and nodes in the networks are analysed.

Key words: deep neural networks, deep learning

Introduction and previous work

In the recent years, artificial neural networks have become one of the preferred tools in data mining (Han et.al, 2011). They are used both in data classification and for modelling and forecasting data (regression analysis). For the past 20 years, researchers at the University of Mining and Geology have been studying the ability of neural networks to analyse data from the mining industry. Topalov and Hristov (2007) examined the possibility and the quality of modelling by neural networks of geological parameters of ore deposit. Data from the operational study of individual horizons in an open pit mine were used. In another work (Topalov, Hristov, 2008) the possibility of predicting a quality indicator in one horizon of an open pit mine with a trained neural network on the data from several previous horizons is evaluated. Further (Hristov, Topalov, 2011) the influence of the sample density on the quality of training of the neural network is studied. The same authors (Hristov, Topalov, 2012) investigated the possibility for application of neural networks in forecasting the extraction in an underground mine. Hristov (2015) and Hristov and Topalov (2015) considered other aspects of such research on mining data.

Some years ago, according to the number of hidden layers, neural networks were divided into single-layer and multilayer ones. Recently, single-layer nets are called shallow, while multilayer networks are referred to as deep networks. In addition, the research on deep neural networks is named deep learning.

The aim of the present study is to determine how the number of hidden layers and the number of neurons in them affect the quality of the analysis of data from ore exploration.

Experimental Framework

The dataset was obtained from the operational study of mining horizon 1015 from the open pit “Ellatsite”. The data includes 1954 instances with the following parameters - coordinates (x, y) of the sample and content of useful indicator copper (Cu).

For the study, a neural network simulator Neural Designer by Artelnics is used.

The experiment is divided into two parts. Firstly, the influence on the quality of the analysis of the number of hidden layers of the neural network is sought.

Once this number of layers has been determined, the second study looked at the effect on quality by changing the number of neurons in the hidden layers.

A regression neural network of Perceptron type is used. The architecture contains two input neurons for the coordinates (x, y) of the instances in the first (input layer), a various number of hidden layers and one neuron for the copper content in the output layer (Figure 1).

![Fig. 1. Neural network architecture: deep neural network (a) and shallow neural network (b)](https://example.com/figure1.png)

The data is divided into three sets: 1174 instances for the training set, 390 instances for the validation set, and 390 instances for the test set (after training). The quasi-Newton method is used here as a training algorithm. Neuron activation function is a hyperbolic tangent. Training stopping criterion is reaching 1000 epochs (iterations) or training maximum time of 1 hour, or 100 epochs without training error decrease. In the first study, the number of neurons in the hidden layers of the network is fixed at 20. The following networks are examined: a shallow network - 20 neurons in the hidden layer, a two-layer network with 10x10 neurons, a three-layer network - 7x7x6 neurons, a four-layer network - 5x5x5x5, a five-layer network - 4x4x4x4x4 and a twenty-layer network - 20 layers with one neuron in each layer.
Based on the results of the first part, and after the optimal number of layers was found, the second study experimented with networks of 2, 4, 6, 8, 10 and 12 neurons in each hidden layer.

**Results and discussion**

The mean value of the useful Cu index in the tested instances is 0.076 and the variance is 0.031. The distribution of Cu is given in Figure 2 and as can be seen it is normal.

The results of the training and the testing of the neural networks from the first study are presented in Table 1. The correlation coefficients were calculated as a ratio between the actual Cu content in the instances and the predicted Cu content calculated by the neural networks. From Figure 3 it is seen that the two-layer network’s correlation provides the best outcome, i.e. the conclusion from the first study is that, with a fixed number of neurons (20), the deep neural network with two hidden layers achieves best quality in modelling and forecasting the discussed geological indicator (Figure 4).

![Fig. 2. Cu distribution](image)

The differences in the correlation coefficients of networks with 4 neurons or more per layer are very close.

![Fig. 3. Correlation coefficients according to the number of hidden layers of the trained neural networks](image)

![Fig. 4. Linear regression of the dependency between actual and predicted Cu contents in a deep neural network with two hidden layers](image)

Therefore, a two-layer network with 4x4 neurons in the hidden layers can be used with the same quality, and it has the simplest architecture (number of neurons and number of connections between them).

### Table 1. First experiment results

<table>
<thead>
<tr>
<th>Number of hidden layers</th>
<th>Training mean squared error</th>
<th>Testing mean squared error</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00033</td>
<td>0.00040</td>
<td>0.562</td>
</tr>
<tr>
<td>2</td>
<td>0.00030</td>
<td>0.00033</td>
<td>0.822</td>
</tr>
<tr>
<td>3</td>
<td>0.00030</td>
<td>0.00035</td>
<td>0.81</td>
</tr>
<tr>
<td>4</td>
<td>0.00028</td>
<td>0.00040</td>
<td>0.785</td>
</tr>
<tr>
<td>5</td>
<td>0.00027</td>
<td>0.00041</td>
<td>0.784</td>
</tr>
<tr>
<td>20</td>
<td>0.00107</td>
<td>0.00101</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Based on the first experiment results, second study was performed on deep neural networks with two hidden layers. Networks with 2, 4, 6, 8, 10 and 12 neurons in each hidden layer were trained. The results are shown in Table 2. The correlations show that the neural network with 10 neurons in a layer gives the most accurate results. On the other hand, the observed deviations between testing and training errors show that networks with 10 and 12 neurons are prone to be overtraining.

### Table 2. Second experiment results

<table>
<thead>
<tr>
<th>Number of neurons</th>
<th>Training mean squared error</th>
<th>Testing mean squared error</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.00060</td>
<td>0.00058</td>
<td>0.587</td>
</tr>
<tr>
<td>4</td>
<td>0.00034</td>
<td>0.00029</td>
<td>0.821</td>
</tr>
<tr>
<td>6</td>
<td>0.00032</td>
<td>0.00032</td>
<td>0.8</td>
</tr>
<tr>
<td>8</td>
<td>0.00030</td>
<td>0.00031</td>
<td>0.81</td>
</tr>
<tr>
<td>10</td>
<td>0.00030</td>
<td>0.00033</td>
<td>0.822</td>
</tr>
<tr>
<td>12</td>
<td>0.00028</td>
<td>0.00031</td>
<td>0.806</td>
</tr>
</tbody>
</table>

### Conclusion

Based on the performed research by comparing deep learning with shallow learning techniques, it can be concluded that the deep neural network with two hidden layers delivers superior quality results compared to the other used neural
networks with various depths (in terms of number of hidden layers).

By varying with the number of the neurons in the two-layer deep network, it is observed that the network with 4 neurons per layer gives the most balanced results: correlation with higher accuracy, lack of overtraining and a simplified structure.

As a main conclusion of the study, it can be assumed that based on the same characteristics, deep neural networks give slightly better results than shallow ones.

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EFFECT OF PRESSURE ON GOLD CYANIDE LEACHING

N. Duru

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ABSTRACT. Although the effect of high oxygen pressure on gold recoveries at elevated slurry temperatures was previously investigated, the sole effect of the pressure at ambient temperatures on cyanide leaching with the presence of nearly enough oxygen for the cyanide reactions to occur has not been found to be studied. This research work was carried out with the objective of investigating the effect of pressure on the recovery of gold from an oxide gold ore and flotation tailing (Carbon in leach (CIL) feed) samples during cyanide leaching process at room temperature. Pressure cyanidation experiments were run in a batch autoclave under different air and nitrogen gas pressures, and pH conditions. Atmospheric bottle roll leach tests for 24 and 8 hours resulted in 90.5% and 68.4% gold recoveries, respectively, whereas 8 hours batch autoclave leach tests under 90 psi air pressure resulted in 88.8% gold recovery from oxide ore samples. Flotation tailing samples leached under atmospheric and under 90 psi air pressure for 8 hours resulted in 16.8% and 34.5% gold recoveries, respectively.

Key words: cyanide, pressure leach, gold

Introduction

The process of cyanidation involves the dissolution of gold containing ores in cyanide solution with the presence of base and oxygen (Park, 1987). During dissolution of gold in cyanide solution, as a first step, oxygen is reduced, and hydrogen peroxide is formed as an intermediate product and hydrogen peroxide becomes the oxidising agent in the second step. The overall chemical reactions are presented below (Senanayake, 2005).

\[
2Au + 4CN^- + O_2 + 2H_2O \rightarrow 2Au(CN)_2^- + 2H_2O + 2OH^- \tag{1}
\]

\[
2Au + 4CN^- + H_2O \rightarrow 2Au(CN)_2^- + 2OH^- \tag{2}
\]

The summation of equations (1) and (2) is presented in the following equation (Elshner, 1986).

\[
4Au + 8CN^- + O_2 + 2H_2O \rightarrow 4Au(CN)_2^- + 4OH^- \tag{3}
\]

In heterogeneous systems, cyanide ions and dissolved oxygen in the slurries will diffuse through the pores of the particles as follows according to the Fick's Law (Habashi, 1967):

\[
\frac{d(O_2)}{dt} = \frac{D_{O_2}}{\delta} \cdot A_1 \cdot \{[O_2]_i - [O_2]_l\} \tag{4}
\]

\[
\frac{d(CN^-)}{dt} = \frac{D_{CN^-}}{\delta} \cdot A_2 \cdot \{[CN^-]_i - [CN^-]_l\} \tag{5}
\]

where \(\frac{d(O_2)}{dt}\), \(\frac{d(CN^-)}{dt}\) - O_2 and CN^- dissolution rate (moles/sec), \(D_{O_2}\), \(D_{CN^-}\) - diffusion coefficients of dissolved oxygen and cyanide (cm^2/sec), \([O_2]_i\), \([CN^-]_i\) - O_2 and CN^- concentration in the solution (moles/ml), \([O_2]_l\), \([CN^-]_l\) - O_2 and CN^- concentration at the interface (moles/ml), \(A_1\), \(A_2\) - surface area where leaching reactions occur (cm^2), \(\delta\) - boundary layer thickness, cm.

Gold is leached within the micropores of the solids where the rate of lixiviant diffusion will be directly affected by its pressure gradient in addition to the boundary layer conditions on the solid surfaces.

Relationship between the pressure gradient and a liquid flow rate into a macroscopic channel that is causing wetting of the pores is shown by the Poiseuille flow as follows (Mott, 2015):

\[
\bar{v} = \frac{D^2}{32 \mu} \cdot \delta p \tag{6}
\]

where \(\bar{v}\) - flow rate average, \(D\) - channel diameter, \(\mu\) - liquid viscosity, \(\delta p\) - pressure gradient.

For the microscopic channel case the capillary effect should also be taken into account for the balance between the applied pressure and the effects of surface tension. This equilibrium is described by the Laplace-Young equation (Ibach, 2006):

\[
\frac{p_{in}}{D} = \frac{4\Delta \gamma}{D} \tag{7}
\]

where \(p_{in}\) - infiltration pressure, \(\Delta \gamma\) - excess-liquid interfacial tension, \(D\) - channel diameter.

As shown on the equations 6 and 7, by the application of the external pressure, lixiviants can be forced into the pores of solid particles which indicates that fluid motion rate on a solid surface is governed by the pressure.

Based on this hypothesis, the research work carried out with the objective of investigating the effect of pressure on the recovery of gold during cyanide leaching process at room temperature.

The testing focused on leaching of ore samples in the presence of pressurised air and nitrogen, while having atmospheric pressure air within vapour space of the batch autoclave at the beginning of each experiment.

All sample preparations and assaying throughout the experimental study were performed utilising industry accepted standards.

Leaching experiments were applied to grab samples of an oxide ore and flotation tailings in order to compare pressure leaching effects on samples of different mineralogical compositions. Pressure leach experiments were run in a two-litre batch autoclave under different air/nitrogen gas pressures and pH conditions.

Experimental

Samples

Experiments were conducted on two different samples, an oxide gold ore and flotation tailings (CIL Feed). Leco analysis for total sulphur, inductively coupled plasma mass spectrometry (ICP-MS), cyanide shake tests with atomic absorption spectrometry (AAS) and fire assaying were conducted on pulverised dry head and leached samples of the oxide ore and flotation tailings.
The oxide ore’s average total gold (AuFA) and cyanide soluble gold (AuCN) contents were 0.222 and 0.213 troy ounce per ton, respectively whereas flotation tailings samples AuFA and AuCN amounts were 0.028 and 0.0124 troy ounce per ton, respectively. Fire assay analyses showed that oxide ore has nearly eight times more gold content than the flotation tailings. The cyanide shake tests showed that 44% of the total gold amount was amenable to cyanide leaching for flotation tailing samples whereas cyanide leachable gold content for the oxide ore samples was 96% of the total gold content. The sulphide sulphur content of the oxide ore and flotation tailings were found as 0.159% and 0.337%, respectively. Test samples are shown on Figure 1 and Figure 2.

Experimental Procedures

Flotation tailings samples had particle size of $P_{80} = 200$ mesh. In order to reduce the size of the oxide ore grab samples, a three-stage crushing-screening and a grinding procedure was applied. Crushed oxide ore product was weighed and fed to the ball mill to reduce its particle size distribution to flotation tailings samples’ size distribution. Following the grinding, the mill product was collected and left to dry in an oven at 35 °C for 24 hours. The dried grind product was used as feed for leaching experiments.

Cyanide leaching experiments were conducted at 25 °C and under 12.4 psi atmospheric pressure, and 30, 60, 90 psi autoclave pressures for 8 hours. Figure 3 and Figure 4 show the experimental setups. Oxide ore were also leached for 24-hour period under atmospheric pressure by bottle roll equipment with the addition of same amount of CaO as in the 8-hour period experiments.

### Table 1. Oxide ore samples

<table>
<thead>
<tr>
<th>Type</th>
<th>Weight</th>
<th>Sample name</th>
<th>Type</th>
<th>Ag (ppm)</th>
<th>Al (ppm)</th>
<th>As (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Head</td>
<td>300 g +</td>
<td>Golden Days oxide ore - head assay</td>
<td>Au/Au ore</td>
<td>3.314</td>
<td>576.658</td>
<td>61.97</td>
</tr>
<tr>
<td>AUCN (OPT)</td>
<td></td>
<td>AUFA1 (OPT)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2126</td>
<td></td>
<td>0.2217</td>
<td></td>
<td>0.0098</td>
<td>18.729</td>
<td>0</td>
</tr>
<tr>
<td>CAI (%)</td>
<td>Ca (ppm)</td>
<td>Cd (ppm)</td>
<td></td>
<td>5.263</td>
<td>224.263</td>
<td>0.048</td>
</tr>
<tr>
<td>0.08</td>
<td>264.081</td>
<td>0.581</td>
<td></td>
<td>53.263</td>
<td>224.263</td>
<td>0.048</td>
</tr>
<tr>
<td>Fe (ppm)</td>
<td>Hg (ppm)</td>
<td>Li (ppm)</td>
<td></td>
<td>434.366</td>
<td>134.883</td>
<td>6.197</td>
</tr>
<tr>
<td>14755.7</td>
<td>0.133</td>
<td>0.003</td>
<td></td>
<td>434.366</td>
<td>134.883</td>
<td>6.197</td>
</tr>
<tr>
<td>Ni (ppm)</td>
<td>Pb (ppm)</td>
<td>P (ppm)</td>
<td></td>
<td>434.366</td>
<td>134.883</td>
<td>6.197</td>
</tr>
<tr>
<td>41.774</td>
<td>6.096</td>
<td>64.337</td>
<td></td>
<td>434.366</td>
<td>134.883</td>
<td>6.197</td>
</tr>
<tr>
<td>SRO (%)</td>
<td>STO (%)</td>
<td>Te (ppm)</td>
<td></td>
<td>434.366</td>
<td>134.883</td>
<td>6.197</td>
</tr>
<tr>
<td>0.051</td>
<td>0.21</td>
<td>14.047</td>
<td></td>
<td>434.366</td>
<td>134.883</td>
<td>6.197</td>
</tr>
</tbody>
</table>

Table 1 and Table 2 show the oxide ore and flotation tailings samples’ elemental analyses. CTOT, CAI, AuPR, SRO, STO are total carbon, organic carbon, preg rob material, sulphate sulphur and total sulphur respectively. Both oxide ore and flotation tailings samples were primarily selected for this experimental test work because of their low sulphide sulphur content. The first set of experiments were planned to be conducted on oxide ore samples with high grade gold content and the second set of experiments with lower gold grade flotation tailing samples.

The high gold content of oxide ore samples provided better observation of recovery changes during the experiments. A second set of experiments were conducted with flotation tailings samples in order to investigate the effect of pressure cyanidation on the recoveries where cyanide soluble gold was relatively lower than the oxide samples.
Table 2. Flotation tailings samples

<table>
<thead>
<tr>
<th>Type</th>
<th>Weight</th>
<th>Sample name</th>
<th>Type</th>
<th>Ag (ppm)</th>
<th>Al (ppm)</th>
<th>As (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leach tails</td>
<td>+100 g</td>
<td>Flotation tailings head assay</td>
<td>Au ore</td>
<td>0</td>
<td>3452.55</td>
<td>976.179</td>
</tr>
<tr>
<td>AUCN (OPT)</td>
<td>0.0124</td>
<td>AUFA1 (OPT)</td>
<td>AUFA2 (OPT)</td>
<td>BA (ppm)</td>
<td>0.243</td>
<td>3.092</td>
</tr>
<tr>
<td>AUPR (OPT)</td>
<td>0.045</td>
<td>2969.37</td>
<td>2.496</td>
<td>6.384</td>
<td>16.219</td>
<td></td>
</tr>
<tr>
<td>Ni (ppm)</td>
<td>12237</td>
<td>Hg (ppm)</td>
<td>Li (ppm)</td>
<td>659.193</td>
<td>45.816</td>
<td></td>
</tr>
<tr>
<td>Fe (ppm)</td>
<td>4.059</td>
<td>2.142</td>
<td>Mg (ppm)</td>
<td>684.768</td>
<td>45.343</td>
<td></td>
</tr>
<tr>
<td>Ni (ppm)</td>
<td>43.713</td>
<td>Pb (ppm)</td>
<td>P (ppm)</td>
<td>684.768</td>
<td>45.343</td>
<td></td>
</tr>
<tr>
<td>Ni (ppm)</td>
<td>0.487</td>
<td>0.824</td>
<td>Te (ppm)</td>
<td>25.354</td>
<td>6.441</td>
<td></td>
</tr>
</tbody>
</table>

During the autoclave leaching experiments, the vessel was pressurised by pure nitrogen gas or air. All leaching experiments were conducted with addition of a base or under natural pH conditions of the samples without addition of a base. Table 3 summarises pressure cyanidation experimental conditions for both ore types at 8-hour leaching period.

Table 3. Autoclave experiments summary

<table>
<thead>
<tr>
<th>Pressure (psi)</th>
<th>Air pressure</th>
<th>Nitrogen pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Base addition</td>
<td>Base addition</td>
</tr>
<tr>
<td>90</td>
<td>None</td>
<td>CaO</td>
</tr>
<tr>
<td>60</td>
<td>CaO</td>
<td>None</td>
</tr>
<tr>
<td>30</td>
<td>CaO</td>
<td></td>
</tr>
</tbody>
</table>

None of the pressurising gases were purged through the pulp inside the autoclave. Pressurising gases were injected to the autoclave through the pressure inlet valve on top of the autoclave head and the gases accumulated above the slurry inside the autoclave.

Nitrogen gas was used as a pressurising agent to minimise effect of increased dissolved oxygen amount in the solution and to be able to observe the pressure effect on gold leaching. However, at the beginning of each experiment, 1350 cm$^3$ of air was present in the empty top portion of the autoclave under atmospheric conditions. The air left in the autoclave was not purged by nitrogen gas out of the autoclave to ensure the presence of enough oxygen for the cyanide leaching reactions to occur.

First set of bottle roll experiments were conducted with NH$_4$OH, NaOH and CaO as pH modifier for leach kinetics comparison purposes. Calcium oxide (CaO) was used as pH modifier for rest of the cyanidation experiments since it is the most common pH modifier of cyanide leaching process in the mining industry. The oxide ore and flotation tailing samples had natural slurry pH values around 8.3 and 6.8, respectively. Due to lower natural pH value of the flotation tailings slurries, higher lime amounts were added to the solutions in order to have similar pH conditions with the oxide ore pressure leaching experiments.

The amount of calcium oxide added during the flotation tailings pressure leaching experiments was 0.55 grams per 400
grams of dry sample feed (2.75 pound per dry short ton of flotation tailings) whereas this amount was 0.2 g CaO for 400 g of dry sample feed (1 pound per dry short ton of ore) for the Golden Days oxide ore. All experiments regardless of sample type were conducted with addition of 0.4 grams of sodium cyanide (NaCN) for 400 g of dry sample (2 pounds for dry short ton of ore). Silver nitrate with p-dimethylaminobenzylidene rhodanine indicator titration was used to measure free cyanide in leach solutions at the end of the tests.

Results and discussion

Grinding experiments

After completing oxide ore crushing with two different size, 5" x 7", 2.25" x 3", jaw crushers and a roll crusher with -10 mesh reduction size, a grinding study was conducted for Golden Days ore samples. Grinding experiments were conducted in order to determine grinding time required to obtain flotation tailings particle size distribution, 80% passing 200 mesh. Total of four grinding experiments were conducted. Experiment results are provided on Figure 5. It was concluded that Golden Days ore samples were to be ground for 48 minutes in order to have flotation tailings samples' particle size, 80% of the particles passing 200 mesh.

![Fig. 5. Golden Days samples – grind study results](image)

Bottle roll experiments

Bottle roll experiments were conducted to determine cyanide leachability of the samples by the industry accepted standard technique. Initial bottle roll and autoclave experiments were conducted for different mixing rates to determine a mixing rate both for autoclave and bottle rolls that would give similar cyanide recovery values for the same leaching time at atmospheric pressure.

As shown on the Table 4, bottle roll tests resulted in recoveries of more than 87% gold recoveries at the end of 24 hours under atmospheric conditions.

Table 4. Golden Days samples 24 h bottle roll gold recoveries under atmospheric pressure of 12.4 psi

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Base type</th>
<th>pH</th>
<th>Mixing rate (rpm)</th>
<th>AuFA Rec. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8BR</td>
<td>CaO</td>
<td>11.7</td>
<td>110</td>
<td>90.5</td>
</tr>
<tr>
<td>6BR</td>
<td>CaO</td>
<td>11.6</td>
<td>98</td>
<td>89.1</td>
</tr>
<tr>
<td>1BR</td>
<td>CaO</td>
<td>11.5</td>
<td>81</td>
<td>87.4</td>
</tr>
<tr>
<td>9BR</td>
<td>NaOH</td>
<td>10.9</td>
<td>110</td>
<td>91.3</td>
</tr>
<tr>
<td>2BR</td>
<td>NaOH</td>
<td>11.1</td>
<td>98</td>
<td>89.0</td>
</tr>
<tr>
<td>5BR</td>
<td>NaOH</td>
<td>11.1</td>
<td>81</td>
<td>88.6</td>
</tr>
<tr>
<td>3BR</td>
<td>NH4OH</td>
<td>10.7</td>
<td>110</td>
<td>93.3</td>
</tr>
<tr>
<td>10BR</td>
<td>NH4OH</td>
<td>10.6</td>
<td>81</td>
<td>89.8</td>
</tr>
</tbody>
</table>

Between 65% to 72% of the total gold (AuFA) contained in Golden Days ore was leached at the end of the 8 h cyanide bottle roll experiments. Bottle roll tests showed that at the end of the 24-hour period 87% of the total gold was recovered by adding CaO as a base and rolling the bottles at 81 rpm. As expected, higher mixing rates resulted in higher gold dissolution rates by reducing diffusion layer thickness and increasing mass transfer rates of oxygen and cyanide during leaching.

As it can be observed from from Figure 6 bottle roll leaching experiments where CaO was used as a base has shown slower gold dissolution kinetics and lower recoveries at the end of the 24 hours leaching period. This can be explained by the retarding effect of the lime on gold dissolution. Formation of calcium peroxyde film on the surface of the gold particles occurs when lime reacts with hydrogen peroxyde (H2O2) in the slurry solution by the following reaction (Barsky,1934)

\[ \text{Ca(OH)}_2 + 2\text{H}_2\text{O}_2 \rightarrow \text{CaO}_2 + 2\text{H}_2\text{O} \]  

Autoclave experiments

Golden Days samples (Oxide ore)

Autoclave experiments were conducted to investigate room temperature pressure cyanidation effects on gold recoveries. Initial autoclave experiments were conducted at 200, 350 and 400 rpm impeller rotational speeds to find the right mixing rates that would give similar recovery values with the bottle roll experiments.
Two hundred (200) rpm rate was not enough to suspend the particles and caused settling of the solid particles to the bottom of the autoclave vessel. The minimum impeller rotational speed was found to be 300 rpm in order to have all solid particles suspending in solutions. Mixing rates for bottle roll and autoclave experiments for the same recoveries were found to be 81 rpm and 400 rpm respectively. Bottle roll experiment #1 had 66.4% of the total recovered after 8 hours of leaching. The gold recoveries increased with the increased pressure levels. The resulting gold recoveries from both bottle roll and autoclave experiments and percent gold recovery increases for the pressure cyanidation experiments are presented on Table 6. The comparison of the recoveries between the bottle roll and autoclave experiments for different pressure levels are presented in Figure 7.

It was expected that increased gold recoveries would result in higher cyanide consumption. But examining all pressure leaching experiments that resulted in higher recoveries, the cyanide usage of these experiments showed lower cyanide consumption compared to bottle roll experiments.

Golden Days ore has natural pH values of 8.3. During gold dissolution by cyanide (Equation 3), the leach solution becomes more basic due to formation of hydroxide ions (OH\(^{-}\)). As a result of this, the pH of the solution for the experiments conducted with Golden Days samples under air pressure without addition of base rose to 10.1 which is very close to the optimum pH value (10.3) for gold cyanide leaching.

The experiments at natural pH values of oxide ore samples which were close to the optimum leaching pH value showed higher gold recoveries compared to the ones conducted with base addition resulting in higher pH and lower NaCN consumption. However, the pH – cyanide consumption – gold recovery relationship observed for the experiments conducted under nitrogen pressure with addition of CaO (Experiment sets 17, 18, 19) and without addition of CaO (Experiment sets 38, 39, 40) were opposite to the ones conducted under air pressure.

The experiments conducted under nitrogen pressure and without any base resulted in higher cyanide consumptions and reduced gold recoveries compared to the experiments conducted with base addition as shown on Table 6.

Prior to pressurising the autoclave, air was present within the empty portion of the autoclave (1350 ml at 12.4 psi) since the air was not flushed out prior to experiments. Following the pressurisation of the autoclave, the dissolved oxygen amount in the slurry would be expected to increase. But the dissolved oxygen amount in the slurry was lower when the reactor was pressurised with pure nitrogen gas compared to when the air was the pressurising agent since the contained oxygen in the pressurised air would cause more oxygen dissolution into the slurry. The higher cyanide consumption and lower gold recoveries observed with no base addition and nitrogen gas pressurisation experiments may be due to the non-optimal [CN\(^{-}\)/O\(_2\)] ratio and pH variations in the slurry causing lower gold dissolution rates and enhancing the decomposition of cyanide due to reactions with other metals, i.e. iron, present in the ore.

**Leaching kinetics**

Golden Days samples leaching kinetic curves of the bottle roll and autoclave experiments are presented on the next four figures. Figure 8 shows the dissolution kinetics of experiments where lime (CaO) was added to the solution and air used as a pressurising agent, whereas Figure 9 shows the gold dissolution kinetics when the nitrogen gas was used as a pressurising agent. The case where applied gas was air without the addition of base into the leach solution is presented on Figure 10.

The leach kinetic curves presented below also point out a higher kinetic rate with the increase in pressure levels. Also all four curves presented show that the gold recovery growths with increased pressure levels are independent from the solution pH values since the pressure effect on gold recoveries mainly resulted from a physical effect (increased lixiviant diffusion rate into the micropores of the solids), not from a chemical effect on the gold dissolution rates.

**Flotation tailings**

Additional experiments with flotation tailings (CIL feed) samples were conducted to compare the pressure effect on recoveries for the samples with different mineralogical composition. The main difference in the results between Golden Days samples and flotation tailings were the overall sample cyanide soluble gold (AuCN) and total gold (AuFA) values.
Experimental results are presented with and without base addition for the leaching of the flotation tails at atmospheric and elevated pressures. The flotation tailing samples had lower natural pH values (around 6.8) compared with Golden Days ore samples. Due to lower natural pH value of the flotation tailings samples, higher lime amounts were added to the solution in order to have similar pH conditions with the Golden Days pressure leaching experiments.

The pressure leaching experiments conducted by adding lime to the leach slurry showed higher gold recoveries than experiments with no base addition due to the increase from the natural pH of the flotation tailings slurry to close to optimum cyanide leaching pH values (10.3).

Pressure cyanidation experiments conducted at pH values less than 10 caused a decrease in gold recoveries and an increase in cyanide consumption compared to experiments conducted with average pH values between 10.6 and 11.0. This could be explained by the effect of the pH values on formation of cyanide species and reactions with other metals consuming cyanide.

On the other hand, most pressure cyanidation experiments at any pH value resulted in higher gold recoveries compared to experiments conducted at atmospheric pressures. As presented on Table 7, gold recoveries increased up to 105% for the same time of leaching at elevated pressure levels (90 psi) compared to the experiments conducted at atmospheric conditions.
Table 7. Flotation Tailings – AuFA Recoveries for 8 h leaching time

<table>
<thead>
<tr>
<th>Exp. No</th>
<th>Press. (psi)</th>
<th>Gas type</th>
<th>Base</th>
<th>NaCN Cons. (lb/st of ore)</th>
<th>Final pH</th>
<th>AuFA Rec. (%)</th>
<th>Δ AuFA Rec. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>12.4</td>
<td>-</td>
<td>CaO</td>
<td>1.76</td>
<td>10.9</td>
<td>16.8</td>
<td>-</td>
</tr>
<tr>
<td>29</td>
<td>90</td>
<td>Air</td>
<td>CaO</td>
<td>1.68</td>
<td>10.6</td>
<td>34.5</td>
<td>105.4</td>
</tr>
<tr>
<td>30</td>
<td>60</td>
<td>Air</td>
<td>CaO</td>
<td>1.36</td>
<td>10.7</td>
<td>29.0</td>
<td>72.6</td>
</tr>
<tr>
<td>44</td>
<td>30</td>
<td>N₂</td>
<td>CaO</td>
<td>1.25</td>
<td>10.6</td>
<td>23.0</td>
<td>36.9</td>
</tr>
<tr>
<td>25</td>
<td>90</td>
<td>N₂</td>
<td>CaO</td>
<td>1.30</td>
<td>10.7</td>
<td>29.7</td>
<td>76.8</td>
</tr>
<tr>
<td>26</td>
<td>60</td>
<td>N₂</td>
<td>CaO</td>
<td>1.58</td>
<td>10.6</td>
<td>25.2</td>
<td>50.0</td>
</tr>
<tr>
<td>43</td>
<td>30</td>
<td>N₂</td>
<td>CaO</td>
<td>1.57</td>
<td>11.0</td>
<td>18.8</td>
<td>11.9</td>
</tr>
<tr>
<td>32</td>
<td>90</td>
<td>Air</td>
<td>-</td>
<td>2.21</td>
<td>8.1</td>
<td>26.8</td>
<td>59.5</td>
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<tr>
<td>33</td>
<td>60</td>
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<td>2.23</td>
<td>8.1</td>
<td>25.9</td>
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<tr>
<td>34</td>
<td>30</td>
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<td>-</td>
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<td>8.0</td>
<td>21.3</td>
<td>26.8</td>
</tr>
<tr>
<td>22</td>
<td>90</td>
<td>N₂</td>
<td>-</td>
<td>2.27</td>
<td>7.7</td>
<td>22.0</td>
<td>30.9</td>
</tr>
<tr>
<td>23</td>
<td>60</td>
<td>N₂</td>
<td>-</td>
<td>2.17</td>
<td>8.4</td>
<td>17.0</td>
<td>1.2</td>
</tr>
<tr>
<td>24</td>
<td>30</td>
<td>N₂</td>
<td>-</td>
<td>2.18</td>
<td>7.9</td>
<td>16.0</td>
<td>-</td>
</tr>
</tbody>
</table>

Pressure cyanidation experiments conducted with air pressure resulted in higher total gold (AuFA) recoveries compared to the experiments where nitrogen gas was used for pressurising the autoclave. Experiment 24 (No base, 30 psi N₂ pressure) and 23 (No base, 60 psi, N₂ pressure) gave similar total gold (AuFA) recoveries when compared to the experiment that was run under atmospheric conditions. This could be caused by combination of low pH and low dissolved oxygen amount in the solution causing lower reaction rates for gold dissolution.

Leaching Kinetics

Figure 11 presents the recoveries on the flotation tailings samples for each pressure level. The leaching kinetic curves of the reactions for different pH and pressure levels are shown on Figures 12 - 14. Kinetic curves for pressure cyanidation of flotation tails also show the same relationship between recoveries and pressure levels as in the oxide ore experimental work, except the experiments when no base was added. Leaching of ore particles is a diffusion-controlled reaction. It was hypothesised that higher pressure levels cause an increase in the lixiviant diffusion in and out of the micropores of the solids. As a result, reaction rates and gold recoveries were higher for the pressure cyanide leaching experiments than the atmospheric leaching conditions at the same time of leaching at room temperature.

Another effect of the increased pressure was the increase in oxygen partial pressures which causes higher dissolved oxygen concentrations in leach solution. Increase in the dissolved oxygen concentration can improve the reaction rates as long as the free cyanide ions are not the limiting factor and the solid particles are suspending in solution with the sufficient amount of leachable metal.

Explaining the recovery increase by the increase in dissolved oxygen amount is a valid argument if applied pressurising gas contains oxygen, which in this case is air. For this reason, to investigate the pure effect of pressure on leachant diffusivity into the solid particle micropores experiments were conducted with a minimal amount of oxygen present for the reactions to complete. An inert gas, pure nitrogen, was added as a pressurising agent for a set of autoclave tests for oxide and flotation tailings samples. The experiments conducted with the nitrogen gas pressure also resulted in higher gold recoveries compared to atmospheric leaching experiments for the same leaching time and proved the pressure effect on the diffusivity during cyanide leaching.
SUSTAINABLE EXTRACTION AND PROCESSING OF RAW MATERIALS JOURNAL, 2021

The rate of gold dissolution increases with the increased Bottle roll leach experiments where lime (CaO) was used as base resulted in lower gold dissolution kinetics compared to the sodium hydroxide (NaOH) due to the retarding effect of lime.

Leach pressure levels experiments can be further applied to non- Higher slurry mixing rates up to a level during cyanidation

The pH level influences gold dissolution rate and the -

-2

-2

Test work showed - Effect of pressure on recoveries cyanide leaching

The oxygen content of the pressurising gas has effect on the pressure effect on the gold dissolution rate for the cyanide soluble gold. The findings of this study are summarised as follows:

- The rate of gold dissolution increases with the increased pressure levels inside the reactor at ambient temperatures.
- Test work showed that cyanide soluble gold was able to be recovered faster under pressure leaching conditions. 8-hour autoclave leaching under 90 psi pressure recovered nearly as much as gold by 24-hour bottle roll leach under atmospheric conditions.
- The oxygen content of the pressurising gas has effect on gold dissolution rates due to partial pressure of the oxygen gas.
- Effect of pressure on recoveries cyanide leaching experiments was observed on cyanide soluble gold amounts for both type of the samples.
- Leach pressure levels and cyanide consumption rates did not have a direct relationship.
- Cyanide consumption rates of pressure cyanidation test work conducted with a base addition was lower compared to the bottle roll test (Exp#1). On the other hand, cyanide consumption was higher for the experiments where a base was not added to the pressure leaching process compared to the bottle roll test (Exp#1).
- The pH level influences gold dissolution rate and the optimum pH level for the gold dissolution were observed between pH values 10.0 and 10.5.
- Higher slurry mixing rates up to a level during cyanidation improve the rate of gold leaching.

Future work

This research has only been undertaken in a batch autoclave. Additional test work in a closed-circuit pilot plant is recommended to determine the impact of a closed-circuit pressurised continuous system on gold recovery values, retention times and industrial applicability of the process.

Additionally, further research on pressure leaching with alternative lixivants such as thiosulfate, thiocyanate, thiourea in both base and acidic solutions should be investigated to determine economic competitiveness of these reagents to cyanide, using this high-pressure process.

The effect of pressure leaching at room temperature should also be investigated on different metallic ores beneficiation processes such as sulphuric acid (H2SO4) leaching of copper ores. These experiments can be further applied to non-conventional methods such as bio-oxidation to investigate various potential process improvements.

Pressure cyanidation leaching experimental work can be further expanded to optimise parameters such as the pulp density, pH, pressure level, leach time, cyanide consumption and dissolved oxygen. At the end of the test work an industry applicable flowsheet can be generated to use this technology.

At very low pH values, HCN gas will be formed during cyanidation process. Since vapour pressure of HCN gas is 100 kPa (14.5 psi) at room temperature (Smith, Mudder, 1991), there is a possibility of the HCN bubbles to be reduced in leach solution and at elevated pressures where HCN will not volatise and thus will stay in solution inside the reactor. Additional pure gold pressure leaching experiments with acidic solution conditions should be conducted to investigate gold dissolution rates by dissolved HCN, its effects on reagent consumptions and on the activity coefficient of the reagent ions.

**References**


Park J. 1897. The cyanide process of gold extraction, Champtaloup and Cooper, Auckland

Senarayake G., 2005. Kinetics and reaction mechanism of gold cyanidation: Surface reaction model via Au(I)-OH-CN, Hydrometallurgy, 80, 2-15

STUDIES ON THE FERRIC IRON SORPTION FROM ACID MINE DRAINAGE ON LEWATIT RESIN AS A STEP FOR METAL CONVERSION TO A VALUE-ADDED PRODUCT

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ABSTRACT. The study aimed to determine the optimal conditions for adsorption and elution of iron from acid mine drainage by ion-exchange resin LEWATIT MonoPlus TP 207 under a batch regime of operation. Langmuir’s sorption equation was employed to analyse the equilibrium data from the experiments. The data fitting demonstrated that the process obeyed pseudo-second-order kinetics with a linear regression coefficient (R²) of 0.9999. Because of the higher demand for hydrochloric solution (100 g/ L) for the ferric iron elution, we studied the effect of the preliminary stage of galvanic elution of Fe(III) to Fe(II) in the presence of H₂. In that way, a slightly acidic solution (30 g/ L) was sufficient to desorb more than 95 % of iron from ion exchange resin LEWATIT MonoPlus TP 207 at a temperature of 70 °C.

Keywords: iron, LEWATIT, sorption, reductive elution

Introduction

As one of the most abundant chemical elements in the Earth’s crust, iron raises a need for adequate control in mining and metallurgical industries. Furthermore, because of its existence in two valency states (ferrous and ferric), both well soluble at acidic pH, iron plays a crucial role in the hydrometallurgical recovery of non-ferrous metals, radioactive elements, precious elements. Higher demand for the groups mentioned above, plus rare-earth metals, was determined by the constant annual growth of the electronic industry mainly. Recent studies showed that some biological and chemical methods could be combined, and thus, it would be possible not only to process raw materials and industrial wastes with complex mineralogy but also to adapt technologies to the stricter environmental regulation (Parhi et al., 2015, Georgiev et al., 2018, Dev et al., 2020).

Mining and metallurgical industries are among industrial branches, which lead to higher iron concentration in freshwater. Consequently, it has both direct and indirect effects on freshwater ecosystems (Vuori, 1995). The direct effects are a consequence of the toxic action of iron compounds (soluble and/or minerals) on the species growth, reproduction, and survival. The indirect effects result from the limited access of organisms to a peculiar ecosystem’s resource, characterised by the relevant quality and quantity.

Three different techniques are applied to control the iron content in laden leach liquors (LLL) and wastewater (Georgiev et al., 2020). The methods for iron precipitation are still the methods most widely applied at industrial scale. The main aim is to precipitate iron to non-toxic ferric iron oxyhydroxide with a crystalline structure and reasonable filtration rate. The main disadvantage is the losses of some valuable metals (up to 13 – 15 %) when the approach is applied to LLL. Magnetite synthesis as a method for iron removal and recovery from solutions is the most promising. The reason for that is the existence of different routes and techniques for mineral synthesis, which strongly affect their particle size, shape, surface, optical and magnetic properties (Kulkarni et al., 2014). It enables the application of magnetite in various fields, ranging from magnetic data storage, biosensing, biomedicine and drug delivery to nano-sorbents in environmental engineering.

Regarding wastewater treatment, especially generated from abandoned mines, the so-called passive system is applied. It is based on chemical and biological processes carried out at an ambient temperature and pressure and iron precipitates as different minerals depending on the maintained environmental conditions (Groudev, 2008).

The other two approaches are based on using highly selective reagents towards some valuable elements from LLL, which enabled their preferential sorption, concentration and elution in its stream lately. The process of solvent extraction relies on a mixture of appropriate diluents (such as kerosene) and suitable organic compounds (some of the organo-phosphorous acids), which form a strong bond with ferric iron from leach liquor (Azizorgahaben et al., 2016). The ion exchange process is an alternative to solvent extraction, and the use of ion-exchange resins prepared from a wide range of synthetic polymers is the basis for this. It determines the ability to produce a wide range of ion exchange resins, each with a specific surface group and charge to adsorb the relevant substance selectively. The first application of ion exchange resins in hydrometallurgy was for uranium recovery from LLL. After developing chelating and impregnated ion exchange resins, their application increased significantly, especially in copper recovery (Davenport et al., 2002). Nowadays, ion exchange resins are applied for non-ferrous, precious, and palladium group metals’ recovery (Ashiq et al., 2019).

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). The presence of aminophosphonic groups on the resin matrix and a negative surface charge determine its ability to extract non-ferrous metals selectivity, even from solutions enriched with inorganic and organic compounds with excellent complexing properties – ammonia, aliphatic and aromatic amines, carboxylic acids, diphosphates, or polyphosphates. The regeneration of ion exchange resin with a suitable inorganic acid starts when more than 75-80 % of its sorption capacity is saturated. In this way, already sorbed non-ferrous metals are desorbed and concentrated in solution with a volume considerably lower than the initial volume of solution (Walting, 2006). The main advantages of using the ion-exchange process for metals recovery is its easiness of operation, no reagent losses, no phases of disengagement, and the lower risk to human health (Nikoloski, Ang, 2014).

This study aimed to determine the optimal conditions for adsorption and elution of iron from acid mine drainage by ion-exchange resin LEWATIT MonoPlus TP 207 under a batch regime of operation.
Materials and methods

Acid mine drainage (AMD) from an abandoned copper mine in Northwest Bulgaria was sampled and analysed in the laboratory. The chemical content and properties of the solution are presented in Table 1.

Effect of the preliminary iron oxidation and precipitation on the ferric iron adsorption by ion exchange resin LEWATIT

The chemical oxidation of ferrous iron was carried out with the serial addition of hydrogen peroxide (30 % solution) and Na₂CO₃ combined with intensive sparging of the solution with air until the pH value in the range of 2.5 – 3.75 is reached. WTW pH-meters equipped with pH-glass and Eh electrodes, assembled with Ag/AgCl reference system and Pt wire, respectively, were used to measure pH and Eh during the chemical oxidation and neutralisation processes. Batch tests for iron sorption were carried out in polypropylene beakers with a volume of 250 mL. LEWATIT MonoPlus TP 207, weak acidic macroporous cation exchange resin with mean bead size 0.61 (± 0.05) mm, was the ion exchange resin used in the study. Initially, 20 g of ion exchange resin was activated with a 100 mL solution containing 100 g/L acid. The stirring rate was 300 rpm, duration – 10 minutes. After the solution separation, the resin washing with water extracted the non-adsorbed acid. Iron sorption started by adding 100 mL of acid mine drainage solution, preliminary treated by chemical oxidation and neutralisation, to the already activated ion exchange resin. The standard conditions for iron adsorption, which applied during the batch tests, if other conditions are not mentioned, were as follows: 300 rpm, 30 °C, aqueous : resin ratio (A: R) = 5:1, agitation time of 10 minutes. A water bath maintained a constant temperature during the experiment. pH equilibrium (pHₑₐ) was measured at the end of the sorption processes. The calculation of iron sorption (D) percentage was according to the equation:

\[
D, \% = \frac{(C₀ - Cₑ)}{C₀} \times 100
\]  

(1)

where: C₀ and Cₑ are the initial and equilibrium iron concentration in the solution before and after sorption (in mg/L), respectively.

Table 1. Chemical content of acid mine drainage

<table>
<thead>
<tr>
<th>Index</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>2.26</td>
</tr>
<tr>
<td>Eh, mV</td>
<td>445</td>
</tr>
<tr>
<td>Acidity, mmol/L</td>
<td>76.3</td>
</tr>
<tr>
<td>Fe, mg/L</td>
<td>3345</td>
</tr>
<tr>
<td>Cu, mg/L</td>
<td>137</td>
</tr>
<tr>
<td>Zn, mg/L</td>
<td>311</td>
</tr>
<tr>
<td>Al, mg/L</td>
<td>183</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>3775</td>
</tr>
</tbody>
</table>

The equilibrium iron content on the ion exchange resin (qₑ, mg/g resin) was found according to the equation:

\[
qₑ = (Cᵢ - Cₑ) \times V / w
\]  

(2)

where: V – a volume of the solution during the sorption test, L; w – the weight of the ion exchange resin, g.

The distribution coefficient (Kᵢ, L/g) of ions between the resin and solution at an equilibrium was quantified by:

\[
Kᵢ = \frac{qₑ}{Cₑ}
\]  

(3)

The separation factor (β) between two ions was quantified by:

\[
β = \frac{Kᵢ₁}{Kᵢ₂}
\]  

(4)

where: Kᵢ₁ and Kᵢ₂ were the distribution coefficient of two ions contained in the solution.

A Langmuir sorption equation was employed to analyse the iron equilibrium data at conditions (pH and temperature) optimal for iron sorption:

\[
\frac{1}{qₑ} = \frac{1}{(Kᵢ x qₑₘₐₓ)} \times \left(\frac{1}{Cₑ}\right) + \frac{1}{qₑₘₐₓ}
\]  

(5)

where: qₑₘₐₓ – maximum content of iron that could adsorb at the relevant experimental conditions, mg/g ion exchange resin, Kᵢ – constant, L/g, qₑₘₐₓ and Kᵢ were calculated according to the following equation:

\[
qₑₘₐₓ = \frac{1}{\text{interception point}}
\]  

(6)

\[
Kᵢ = \frac{1}{\text{slope x qₑₘₐₓ}}
\]  

(7)

where: interception point and the slope were the parameters of a line of 1/ Cₑ versus 1/qₑ.

First and second-order rate equations evaluated the effect of pH and temperature on the iron sorption on ion exchange resin LEWATIT (Ho et al., 2000).

Iron desorption from loaded ion exchange resin LEWATIT MonoPlus TP 207

The iron desorption from the loaded ion exchange resin Lewatit MonoPlus TP 207 was studied at oxidative or reductive conditions. The desorption agent at oxidative conditions consisted of hydrochloric acid with a concentration of 60 – 120 g/L. Aqueous : resin ratio (A: R) applied for the iron desorption was in the range of 2.5 : 1 to 1.5 : 1, and the other conditions were the same as the conditions described for iron sorption.

The reductive elution of iron was carried out in the presence of H₂, and it took place in a tightly closed three-necked flask that contained the resin loaded with iron. The diluted acid solution (20 – 60 g HCl/ L) was added to the flask after oxygen removal by sparging with N₂. In order to ensure Fe⁴⁺ reduction to Fe⁰⁺, the galvanic iron elution was carried out by the flask sparging with H₂. A water bath maintained a constant temperature during the process. The duration of the reductive elution was in the range of 20 – 40 minutes.

Copper ammonia method was used for the copper content determination of the solutions. The selective complexation of ferrous and total iron with 5-sulfosalicylic acid at acidic and alkaline pH determined the ferrous and ferric iron concentration at acidic and alkaline pH (APHA, 1995). The intensity of formed complexes was measured at the relevant wavelengths by spectrophotometer MERCK SQ22.

Results and discussion

Iron concentration in acid mine drainage was higher than the concentration of other metals present in the solution. The ferrous ion was the main iron valency state in the tested solution because the solution drained through the ore body, and the low
concentration of molecular oxygen limited the activity of indigenous chemolithotrophic bacteria with iron-oxidising ability. It is well-known that ion exchange resins adsorb ferrous ions non-selectively, and the process is not efficient in the presence of other divalent cations, especially copper and zinc (Fatima et al., 2020). For that reason, preliminary chemical oxidation and neutralisation of AMD was applied to oxidise the ferrous ions into a ferric state. 

It is well-known that ion exchange resins adsorb ferrous ions non-selectively, and the process is not efficient in the presence of other divalent cations, especially copper and zinc (Fatima et al., 2020). For that reason, preliminary chemical oxidation and neutralisation of AMD was applied to oxidise the ferrous ions into a ferric state. H₂O₂ was used, and we calculated its amount according to the reaction:

\[
2\text{Fe}^{2+} + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + 2\text{H}_2\text{O}
\] (8)

Sodium carbonate was added as an alkalisising agent to the solution when redox potential was higher than + 550 (mV). It enhanced the ferric iron precipitation mainly as goethite (β-FeOOH):

\[
\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{FeOOH} + 3\text{H}^+
\] (9)

At pH > 3.00, the intensive sparging of the pulp with air enhanced the chemical oxidation of the residual concentration of ferrous iron:

\[
\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + 2\text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}
\] (10)

The final pH point of chemical neutralisation significantly affected the ferric iron adsorption by ion exchange resin (Table 2). For example, the lowest equilibrium concentration of iron in solution after the adsorption was measured when the final pH of neutralisation was 3.5. Furthermore, further addition of alkalisising agent during the chemical neutralisation negatively affected the iron adsorption due to the enhanced adsorption of other cations from the solution.

Initially, the chelating resin adsorbed bivalent cations present in the solution. This process acted as a source of hydrogen ions from the resin to the solution, which initiated the goethite dissolution and ferric iron ions accumulated into the solution:

\[
\text{FeOOH} + 3\text{H}^+ \rightarrow \text{Fe}^{3+} + 2\text{H}_2\text{O}
\] (11)

The higher charge of ferric ions enhanced their selective adsorption on the surface of chelating resin compared with the adsorption of presented bivalent cations. At such conditions, the reaction could describe the ferric iron adsorption on chelating resin and the following ion exchange with hydrogen ions:

\[
\text{Fe}^{3+} + 6\text{(HR)} \rightarrow 2(\text{FeR}) + 6\text{H}^+
\] (12)

Table 2. Effect of the equilibrium pH on the iron sorption on ion-exchange resin LEWATIT MonoPlus TP 207*

<table>
<thead>
<tr>
<th>pH of AMD after chemical oxidation and neutralisation</th>
<th>Equilibrium pH</th>
<th>Equilibrium concentration of iron, Cₓ, mg/L</th>
<th>Equilibrium concentration of copper, Cᵧ, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.50</td>
<td>1.23</td>
<td>481.5</td>
<td>24.1</td>
</tr>
<tr>
<td>3.00</td>
<td>1.48</td>
<td>291</td>
<td>16.2</td>
</tr>
<tr>
<td>3.50</td>
<td>1.63</td>
<td>40</td>
<td>12.2</td>
</tr>
<tr>
<td>3.75</td>
<td>1.91</td>
<td>112.5</td>
<td>9.5</td>
</tr>
</tbody>
</table>

* All experiments were carried out at a temperature of 30 °C

Table 3. Effect of the equilibrium pH on the separation between iron and copper adsorption on ion-exchange resin LEWATIT MonoPlus TP 207*

<table>
<thead>
<tr>
<th>Equilibrium pH</th>
<th>Distribution coefficient of iron, Kₓ, L/ g</th>
<th>Distribution coefficient of copper, Kᵧ, L/ g</th>
<th>Separation factor (β), Kₓ/Kᵧ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.23</td>
<td>0.30</td>
<td>0.22</td>
<td>1.36</td>
</tr>
<tr>
<td>1.48</td>
<td>0.52</td>
<td>0.36</td>
<td>1.44</td>
</tr>
<tr>
<td>1.63</td>
<td>4.13</td>
<td>0.49</td>
<td>8.43</td>
</tr>
<tr>
<td>1.91</td>
<td>1.44</td>
<td>0.65</td>
<td>2.21</td>
</tr>
</tbody>
</table>

* All experiments were carried out at a temperature of 30 °C

Table 4. Effect of the temperature on the iron sorption on ion-exchange resin LEWATIT MonoPlus TP 207*

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Equilibrium pH</th>
<th>Equilibrium concentration of iron, Cₓ, mg/L</th>
<th>Equilibrium concentration of copper, Cᵧ, mg/L</th>
<th>Efficiency of iron sorption, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.17</td>
<td>625.3</td>
<td>81.3</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1.2</td>
<td>347.8</td>
<td>89.6</td>
<td></td>
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<tr>
<td>30</td>
<td>1.63</td>
<td>40</td>
<td>98.8</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>1.61</td>
<td>50.2</td>
<td>98.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 5. Effect of the ion exchange resin’s amount on the ferric iron sorption

<table>
<thead>
<tr>
<th>LEWATIT amount, g</th>
<th>Cₓ, mg/L</th>
<th>qₓ, mg/g</th>
<th>The efficiency of iron adsorption, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2515</td>
<td>16.60</td>
<td>24.8</td>
</tr>
<tr>
<td>10</td>
<td>1682</td>
<td>16.63</td>
<td>49.7</td>
</tr>
<tr>
<td>15</td>
<td>890</td>
<td>16.37</td>
<td>73.4</td>
</tr>
<tr>
<td>20</td>
<td>40</td>
<td>16.53</td>
<td>98.8</td>
</tr>
<tr>
<td>25</td>
<td>13.4</td>
<td>13.33</td>
<td>99.6</td>
</tr>
</tbody>
</table>

Table 6. Kinetic parameters of iron adsorption on ion-exchange resin LEWATIT MonoPlus TP 207 determined by pseudo-first-order and pseudo-second-order equation rate

<table>
<thead>
<tr>
<th>Pseudo-first order equation rate</th>
<th>Slope</th>
<th>Intercept</th>
<th>qₑ, mg/g</th>
<th>Kₛ, min⁻¹</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.4289</td>
<td>2.2918</td>
<td>9.9827</td>
<td>-0.0429</td>
<td>0.8274</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pseudo-second order equation rate</th>
<th>Slope</th>
<th>Intercept</th>
<th>qₑ, mg/g</th>
<th>Kₛ, g.mg⁻¹.min⁻¹</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0556</td>
<td>0.049</td>
<td>17.9856</td>
<td>0.0631</td>
<td>0.9999</td>
<td></td>
</tr>
</tbody>
</table>
different amounts of resin enabled the determination of the main adsorption process’s characteristics through a Langmuir equation. For example, at the optimal conditions (equilibrium pH 1.63 and temperature of 30 °C), the calculated maximum ferric iron adsorbed on the resin was 16.6 mg/ g resin. Its value was almost equal to the experimentally determined equilibrium iron content (q max) on the resin at the end of the adsorption process (16.53 mg/ g resin, Table 5). The distribution coefficient value of ferric iron (k d) determined by the Langmuir equation was 3.87, and it was similar to the value of the distribution coefficient (k d) determined experimentally (4.13, Table 3). Zhang et al. (2016) determined an almost equal value for q max (16.33 mg Fe/ g resin) when studied the ferric iron extraction from synthetic copper solution with hydroxy-oxime chelating resin.

The efficiency of iron adsorption in the presence of different amounts of resin enabled the determination of the main adsorption process’s characteristics through a Langmuir equation. For example, at the optimal conditions (equilibrium pH 1.63 and temperature of 30 °C), the calculated maximum ferric iron adsorbed on the resin was 16.6 mg/ g resin. Its value was almost equal to the experimentally determined equilibrium iron content (q max) on the resin at the end of the adsorption process (16.53 mg/ g resin, Table 5). The distribution coefficient value of ferric iron (k d) determined by the Langmuir equation was 3.87, and it was similar to the value of the distribution coefficient (k d) determined experimentally (4.13, Table 3). Zhang et al. (2016) determined an almost equal value for q max (16.33 mg Fe/ g resin) when studied the ferric iron extraction from synthetic copper solution with hydroxy-oxime chelating resin.

Table 7. Effect of the hydrochloric content on the iron elution from loaded ion-exchange resin LEWATIT MonoPlus TP 207*

<table>
<thead>
<tr>
<th>Content of HCl in desorption solution, g/L</th>
<th>Fe in solution, mg/L</th>
<th>The efficiency of iron desorption, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>2405</td>
<td>36.4</td>
</tr>
<tr>
<td>60</td>
<td>4335</td>
<td>65.6</td>
</tr>
<tr>
<td>80</td>
<td>6160</td>
<td>93.2</td>
</tr>
<tr>
<td>100</td>
<td>6370</td>
<td>96.4</td>
</tr>
</tbody>
</table>

* All experiments were carried out at a temperature of 30 °C

Table 8. Effect of the hydrochloric content on the galvanic elution of iron from loaded ion-exchange resin LEWATIT MonoPlus TP 207*

<table>
<thead>
<tr>
<th>Content of HCl in desorption solution, g/ L</th>
<th>Fe in solution, mg/L</th>
<th>The efficiency of iron desorption, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2150</td>
<td>32.5</td>
</tr>
<tr>
<td>20</td>
<td>4550</td>
<td>68.8</td>
</tr>
<tr>
<td>30</td>
<td>6370</td>
<td>96.4</td>
</tr>
<tr>
<td>40</td>
<td>6490</td>
<td>98.8</td>
</tr>
</tbody>
</table>

* All experiments were carried out at a temperature of 70° C

Table 9. Effect of the temperature on the galvanic elution of iron from loaded ion-exchange resin LEWATIT MonoPlus TP 207*

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Fe in solution, mg/L</th>
<th>The efficiency of iron desorption, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>3790</td>
<td>57.3</td>
</tr>
<tr>
<td>50</td>
<td>5260</td>
<td>79.6</td>
</tr>
<tr>
<td>60</td>
<td>5925</td>
<td>89.6</td>
</tr>
<tr>
<td>70</td>
<td>6370</td>
<td>96.4</td>
</tr>
<tr>
<td>80</td>
<td>6395</td>
<td>96.7</td>
</tr>
</tbody>
</table>

* HCl content in the desorption solution was 30 g/ L

Table 10. Effect of the duration on the galvanic elution of iron from loaded ion-exchange resin LEWATIT MonoPlus TP 207*

<table>
<thead>
<tr>
<th>Duration, minutes</th>
<th>Fe in solution, mg/L</th>
<th>The efficiency of iron desorption, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4840</td>
<td>73.3</td>
</tr>
<tr>
<td>30</td>
<td>6370</td>
<td>96.4</td>
</tr>
<tr>
<td>40</td>
<td>6488</td>
<td>98.2</td>
</tr>
</tbody>
</table>

* All experiments were carried out at a temperature of 70° C and in the presence of 30 g HCl/L

Riveros (2004) has shown that the resins’ ability to adsorb ferric iron strongly depends on their matrix morphology and the surface groups’ acidity. For example, gel-type resins do not adsorb large amounts due to the very low rate of Fe³⁺ diffusion. In contrast to the macroporous acrylic resins, where that effect does not exist, ferric iron is extracted efficiently and selectively. The presence of other competitive cations also affects the resin adsorption capacity to iron. For example, a study carried out by Millar et al. (2015) showed that q max of strong acid cation resin toward ferric iron from solution with no presence of other cations was higher than 47.1 mg/ g resin.

The results from kinetic experiments carried out at the optimal conditions for the iron adsorption show that the process better fits the pseudo-second-order equation rate.

Table 11. Effect of the aqueous : resin (A : R) ratio on the galvanic elution of iron from loaded ion-exchange resin LEWATIT MonoPlus TP 207*

<table>
<thead>
<tr>
<th>Aqueous : resin (A : R) ratio</th>
<th>Fe in solution, mg/L</th>
<th>The efficiency of iron desorption, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 : 1</td>
<td>6550</td>
<td>99.1</td>
</tr>
<tr>
<td>2.0 : 1</td>
<td>7285</td>
<td>88.2</td>
</tr>
<tr>
<td>1.5 : 1</td>
<td>8135</td>
<td>74.2</td>
</tr>
</tbody>
</table>

* The duration of galvanic elution of iron for all experiments was 60 minutes

For example, the value of equilibrium iron content on the resin determined by that equation was 17.98 mg/ g resin (Table 6), compared to the experimentally determined value of 16.53 mg/ g. The linear regression coefficient (R²) value was 0.9999, and the straight line that expressed the kinetic function of t versus t/ q, passed through all experimentally determined dots (Figure 1). On the other hand, the value of equilibrium iron...
content (qₑ) determined by pseudo-first-order equation rate was 9.98 mg/g.

Iron desorption from loaded ion-exchange resin LEWATIT
The opposite process – the process of the iron desorption took place in a solution with acidic pH (Table 7). Apart from the regeneration of the adsorptive properties of the chelating resin, the resin elution played a role in increasing ferric iron concentration in the solution multifold by decreasing the value of the applied aqueous: resin ratio. For that reason, the efficiency of iron desorption was a key parameter for the process characterisation. Therefore, we studied two approaches for the iron desorption from loaded ion-exchange resin LEWATIT MonoPlus TP 207 based on hydrochloric acid as a desorption agent. Hydrochloric acid was used because ferric iron precipitated as akaganeite (γ-FeOOH) in the next step after adding an alkalisising agent and pH correction to a value higher than 3.0. The akaganeite is a precursor for magnetite (Fe₃O₄) synthesis in an oxygen-free milieu and at an appropriate concentration of ferrous iron.

Iron desorption with a solution with a high content of HCl
The higher acid concentration in the desorption solution enabled breaking the chemical bonds between the adsorbed ferric ions and the negatively charged functional groups of the chelating resin to carry out at a higher rate. Therefore, the efficiency of iron desorption strongly depended on the acid concentration in the solution. For example, more than 90 % of iron desorbed when the concentration of hydrochloric acid in the desorption solution was higher than 75 g/L (Table 7). The kinetic of iron desorption with a highly acidic solution was not temperature-dependent, and the process efficiency was acceptable even at a temperature of 10 °C. However, the efficiency of iron desorption dropped significantly if the value of applied A:R was lower than 2.5:1. So, the ferric iron concentration from acid mine drainage increased twofold when ferric ion sorption on LEWATIT MonoPlus TP 207 resin was combined with a desorption stage in the presence of a desorption solution with higher hydrochloric acid content.

Galvanic elution of iron from the loaded ion-exchange resin LEWATIT
The second approach tested relied on the preliminary ferric iron reduction. A wide range of different reducing compounds – gaseous (SO₂ (Majima et al., 1985), H₂ (Demopoulos, Gefvert, 1984), organic (oxalic acid (Zhang et al., 2016)), and inorganic compounds (Zn° (Lupi, Pilone, 2000); SiO₂° (Batelhão-Junior et al., 2019)) could be used for that purpose. H₂ was the reducing substance used in this study, and the main aim was to reduce ferric iron to ferrous state preliminary:

\[ 2\text{Fe}^{3+} + \text{H}_2 \rightarrow 2\text{Fe}^{2+} + 2\text{H}^+ \]  
(13)

In that case, the functional groups of chelating resin held the ferrous iron with weak chemical bonds that broke quickly in the presence of a slightly acidic solution. The hydrogen ions generated during the galvanic reaction of ferric iron took part in the desorption of its ferrous state counterpart. So, an acceptable level of the iron galvanic desorption was reached (above 96 %, Table 8) only in the presence of 30 g/L hydrochloric acid. The main plus of galvanic iron desorption was the lower consumption of acid and an alkalisising agent at the next stage of rich-in-iron pregnant leach solutions processing. The galvanic desorption of iron, however, was a strongly temperature-dependent process. For example, the process efficiency was lower than 60 % at room temperature, and the value of desorption reached almost 80 % at a temperature of 50 °C (Table 9). If only the temperature was maintained at 70 °C or higher, the efficiency of the galvanic iron elution was comparable to the efficiency determined with a desorption solution at a highly acidic pH. The galvanic iron elution was a time-dependent process. It resulted from the presence of a heterogeneous mixture consisting of three phases (gaseous, solid, and aqueous) and the relevant surface-controlled processes carried out in pairs between them. Because of the lower kinetic of the galvanic iron reduction, the rate-limiting process received the optimal value of iron desorption after 30 minutes of the process duration (Table 10). We obtained higher iron concentration in the desorption solution when galvanic iron reduction occurred at an A:R ratio lower than 2.5:1. However, it was needed to increase the process duration to an hour in that case (Table 11).

Conclusions
The ferrous iron oxidation to ferric state was a compulsory preliminary process that made possible the iron adsorption from acid mine drainage by ion exchange resin LEWATIT MonoPlus TP 207 to carry out with a higher rate and selectively at the value of 1.63 for equilibrium pH. The maximum amount of ferric iron adsorbed on the ion-exchange resin was 16.6 mg/g resin when the conditions at which the process took place were equilibrium pH 1.63, the temperature of 30 °C, aqueous: resin ratio (A:R) 5:1, and agitation time of 10 minutes. The optimal conditions for galvanic elution of ferric iron from the loaded ion-exchange resin LEWATIT MonoPlus TP 207 in the presence of H₂ and at A:R of 2.5:1 were 30 g HCl/L, the temperature of 70 °C, and duration of 30 minutes. This iron desorption method enabled the resin regeneration to be carried out with insignificant hydrochloric acid consumption.

Acknowledgements. The authors would like to express their gratitude to the Scientific Research & International Partnership Unit at the University of Mining and Geology “St. Ivan Rilski”, Sofia (under GPF-229/2020 project) which supported this study.

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Lupi C., Pilone D., 2000. Reductive stripping in vacuum of Fe(III) from D2EHPA, Hydrometallurgy, 57, 201–207.
SUSTAINABLY DEVELOPING MINING, BENEFICIATION AND METALLURGICAL ENTERPRISES ACCORDING TO UN AND EU REQUIREMENTS

Lyubomir S. Ilchev, Nadezhda G. Davcheva-Ilicheva

Retired, Bulgaria, Sofia 1111, Schipchenski prohod Str. 11, Email: lubomirilchev@abv.bg; Email: davcheva_ilcheva@abv.bg

ABSTRACT: Sustainable development helps the transition of industrial enterprises from "open" to "closed" type of economy, solving their contradictions with the environment and the biosphere. Therefore, the future belongs to those industrial plants that will comply with and put into practice the concept of sustainable development. The authors propose a conditional structural and functional schemes for mining, beneficiation and metallurgical enterprises in accordance with the requirements of the main UN and EU documents for sustainable development. Management, as a major production factor, together with one of its main tools - feedback, have the task to change the ongoing processes to this desired goal. A network of industrial indicators accounting for the effectiveness of systems management and the progress made is also pointed out.

Key words: sustainable development, structure, organisation, functioning, management toolkit.

Introduction

Like most anthropogenic systems, industrial enterprises are structured, organised and operate on a "linear" basis, i.e. as an "open" type of economy, carrying with it huge risks and disadvantages.

Sustainable development (SD) - development in harmony with the environment, in a market economy solves problems such as: quality, material and energy efficiency, waste, markets, prices, problems in the social sphere. It helps the transition of industrial enterprises from "open" to "closed" type - circular economy. The future therefore lies with those industrial enterprises which will comply with and put into practice the concept of sustainable development (Ilchev, 2018).

Requirements of sustainable development to the structure and organisation of mining, beneficiation and metallurgical enterprises

Industrial plants must be structured in such a way as to perform well their main specific objectives and tasks. Sustainable development imposes some additional requirements on their structure and organisation, in order to improve their internal strengths and opportunities for development and strengthen their viability. These requirements in terms of the main factors of production are (Ilchev, 2018):
- conservation and proper management of natural resources and raw materials;
- continuous increase of energy efficiency;
- introduction of non-waste, environmentally friendly technologies;
- environmental protection (EP);
- achieving management for sustainable development of plants.

It is necessary for their organisation to comply with the basic principles of sustainable development. More important of them are (Brundtland, 1987; Davcheva-Ilicheva, Ilchev, 2005):
- Integrity - uniting the economic and social development of the mining, beneficiation and metallurgical plants with the protection and development of the environment. This means that the problems of protecting and improving the environment must be an integral part of those related to the development of raw materials, energy, technology and management.
- Synergy - important for the three main pillars of sustainable development - economic, social and environmental, one of the most influential but also the most underestimated principle of modern development of the information society. For mining, beneficiation and metallurgy, synergy must be achieved both between the main production factors for the sustainable development of plants and throughout the value chain.
- Homeostasis - an important organisational principle for industrial systems, allowing plants in today's dynamic conditions of a constantly changing environment to be maintained, to be internally stable and to develop sustainably. The organisation must help them, like the ecosystems in the biosphere, to self-regulate and self-control. This is possible when there is well-organised feedback in the system.
- Succession - plants should not exclude it, but provide and encourage it, similar to the development in the biosphere. Their inertia must be overcome and the structural elements, and if necessary entire systems, that hold back their sustainable development must be quickly replaced. The goal is to continuously improve their competitiveness and sustainability, regardless of changes in external conditions, such as climate and others.

Conditional functional diagram of sustainably developing industrial enterprises

The conditional functional diagram of a sustainably developing metallurgical plant (on the example of copper pyrometallurgy and / or production of semi-finished products), elaborated by us, is shown in Figure 1. It contains all structural elements, some of them specific for productions upstream and downstream the Raw materials added value chain. There are high requirements and strict control over incoming raw materials, energy and other important resources. Continuous improvement of their quality is required. Important for the sustainable development of plant is the use of "green" energy, full utilisation of waste energy and, if possible, the use of its own alternative energy from renewable sources with the application of modern co- and three-generative energy systems.
The production capacity of the plant must be constantly balanced with the market needs and capabilities of the feeding systems. Its production and technological schemes should be resource and energy efficient, subject to the principle of prevention, recovery or, in extreme cases, harmless disposal of waste. Recycling, recovery and purifying systems serve to prevent and minimise waste, and should be able to generate new by-products.

Final emissions and waste in terms of quality and quantity must be non-adverse for the environment, within the limits of its absorbing and neutralising possibilities. Waste storage facilities must be designed in such a way as to create opportunities for further additional treatment of the waste deposited in them, with the possible creation of new innovative technologies for this purpose.

The quantity and quality of the produced products must meet the high market needs and requirements, ensuring and maintaining high competitiveness of the plant.
Management including feedback - a key factor for achieving sustainable development

The management of the plant has the task to change the ongoing processes according to the changing environment and social requirements for sustainable economic development – Figure 2.

Economic conditions should help the plant management in innovative solutions, to change the existing market relations and requirements in the direction of sustainable development (Figure 2 - the dotted line Sustainable Development and Environmental Protection - SD & EP).

Fig. 2. Conditional functional scheme for sustainable management of an industrial system

Industrial indicators accounting for the effectiveness of systems management and the progress made

A management toolkit for sustainable development is in the early stages of building up. It was launched by the Scientific Advise Group (SAG) - an EU Expert Group, which has developed and proposed a network of important industrial sustainability indicators, with units of measurement (Eurostat, 2010).

We complimented a SAG’s set of indicators with some common and specific indicators and units of measurements concerning branches with pressure upon environment such as mining, beneficiation and metallurgy (Ilichev, Davcheva-Ilicheva, 2015). They are consistent with the most important areas of pressure on the environment from these enterprises - Tables 1 - 5.

Table 1. Indicator for climate changes

<table>
<thead>
<tr>
<th>Indicator branch</th>
<th>Unit of measurement</th>
<th>Proposed by</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emissions of CO₂: open pit mine metallurgy</td>
<td>tones/yr kg/ton of raw material kg/ton of product</td>
<td>SAG authors authors</td>
</tr>
</tbody>
</table>

Table 2. Indicators for air pollution

<table>
<thead>
<tr>
<th>Indicator branch</th>
<th>Unit of measurement</th>
<th>Proposed by</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emissions of SO₂: metallurgy</td>
<td>tones/yr kg/ton of raw material kg/ton of product</td>
<td>SAG authors authors</td>
</tr>
<tr>
<td>Emissions of NOₓ: open pit mine metallurgy</td>
<td>tones/yr kg/ton of raw material kg/ton of product</td>
<td>SAG authors authors</td>
</tr>
<tr>
<td>Emissions of dusts: open pit mine metallurgy</td>
<td>tones/yr kg/ton of raw material kg/ton of product</td>
<td>SAG authors authors</td>
</tr>
<tr>
<td>Emissions of heavy and toxic metals (Cu, Pb, As, Cd, etc.): metallurgy</td>
<td>kg/ton of product</td>
<td>authors</td>
</tr>
<tr>
<td>Fugitive emissions*: open pit mine beneficiation metallurgy</td>
<td>tones/yr</td>
<td>authors</td>
</tr>
</tbody>
</table>

* Indicators have to be introduced after adoption of a proper method for their measurement
Table 3. Indicators for resource depletion

<table>
<thead>
<tr>
<th>Indicator branch</th>
<th>Unit of measurement</th>
<th>Proposed by</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extraction of ore mine</td>
<td>tones/yr</td>
<td>authors</td>
</tr>
<tr>
<td>Depletion of deposits mine</td>
<td>%</td>
<td>authors</td>
</tr>
<tr>
<td>Lost earth open pit mines</td>
<td>tones/yr</td>
<td>authors</td>
</tr>
<tr>
<td>Concentrates beneficiation</td>
<td>tones/yr</td>
<td>authors</td>
</tr>
<tr>
<td>Processed concentrates metallurgy</td>
<td>tones/yr</td>
<td>authors</td>
</tr>
<tr>
<td>Production of non-ferrous metals from ore concentrates metallurgy</td>
<td>tones/yr</td>
<td>SAG</td>
</tr>
<tr>
<td>Increase in territory permanently occupied by infrastructure and waste-tipping mine; beneficiation metallurgy</td>
<td>ha/yr</td>
<td>SAG</td>
</tr>
<tr>
<td>Increase in territory destroyed by extraction mine</td>
<td>ha/yr</td>
<td>authors</td>
</tr>
<tr>
<td>Use of fossil fuels mine metallurgy</td>
<td>toe/ton of raw material/toe/ton of product</td>
<td>authors</td>
</tr>
<tr>
<td>Surface water abstraction beneficiation metallurgy</td>
<td>m³/yr</td>
<td>SAG authors</td>
</tr>
<tr>
<td>Ground water abstraction beneficiation metallurgy</td>
<td>m³/yr</td>
<td>SAG authors</td>
</tr>
</tbody>
</table>

Table 5. Indicators for water pollution & water resources

<table>
<thead>
<tr>
<th>Indicator branch</th>
<th>Unit of measurement</th>
<th>Proposed by</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emissions of organic substances beneficiation</td>
<td>g/m² of water</td>
<td>SAG authors</td>
</tr>
<tr>
<td>Emissions of heavy and toxic metals (Cu, Pb, As, Cd etc.): mine; beneficiation metallurgy</td>
<td>g/m² of water</td>
<td>authors authors</td>
</tr>
<tr>
<td>Acid emissions (SO₄) mine; beneficiation metallurgy</td>
<td>km³/yr</td>
<td>authors</td>
</tr>
<tr>
<td>Waste waters mine; beneficiation metallurgy</td>
<td>m³/ton of raw material/m³/ton production</td>
<td>authors authors</td>
</tr>
<tr>
<td>Water recycling beneficition metallurgy</td>
<td>km³/yr</td>
<td>SAG authors</td>
</tr>
<tr>
<td>Total of waste water treated by industry/total quantity of water used mine; beneficiation metallurgy</td>
<td>%</td>
<td>SAG</td>
</tr>
<tr>
<td>Recycled water/total water used beneficition; metallurgy</td>
<td>%</td>
<td>authors</td>
</tr>
</tbody>
</table>

The industrialisation of a given area must be preceded by preliminary environmental background studies on the state of nature, its resources and the environment, which should be the basis for determining the environmental pressure of the realised production activity.

In a market economy, additional environmental friendly investments in production and output must generate added value for the plant. They need to have an exact economic equivalent and find a place in the most important economic indicators for the functional activity of plant (Keneth et al., 1992; Perloff, van’t Veld, 1994; Aspola, 2008):

- **Profit** Ratio;
- \[ \text{ROCE} = \frac{\text{Pre-tax Operating Profit}}{\text{Capital Employed}} \]
- \[ \text{Return on Investments} = \frac{\text{Profit on Investments–Investments Costs}}{\text{Investments Costs}} \]
- Online time (% of available time).

**Conclusion**

Analyses for harmonious development of the enterprises with nature are in the initial stage. With the help of systematic observations and research in these areas, a cadastre of environmental problems for industry can be created on a
regional and national scale. This will help unite efforts to address the problems and achieve environmentally friendly and sustainable operation of mining, beneficiation and metallurgy.

The functional schemes for sustainable development of mining, beneficiation and metallurgical enterprises elaborated by us contribute to their harmonisation with the surrounding environment and the introduction of a circular economy. The network of indicators describing pressure on the environment provides an opportunity to control the efficiency of the entire technological chain and increases the branch competitiveness.

The management tools for sustainable development proposed by us must be developed and enriched according to the specifics of the respective production.

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THE EUROPEAN GREEN DEAL AND ITS IMPACT ON THE RAW MATERIAL INDUSTRY

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ABSTRACT. Climate changes and environmental degradation are a threat to the existence of Europe and the world. To overcome these challenges, at the end of 2019, the European Commission outlined as a main political line the proposal for the European Green Deal. In most of its aspects, this document is a benchmark for a new mindset that aims to turn the EU in a fair and prosperous society with a modern, resource-efficient and competitive economy in which there will be no net greenhouse emissions in 2050 and the economic growth will not depend on the use of resources. This publication reflects the path from the emergence of the idea of the European Green Deal to the policies pursued today. The academic papers developed in the field are analysed, as well as the prerequisites and challenges that lead to its implementation. An attempt has been made to answer questions related to the main goals of the Green Deal and how these aims correspond to the raw material industry which will be the industry with the most significant consequences in the next decade.

Key words: European Green Deal, raw material industry

State of the art and development of the idea of a European Green Deal

From 1970 to 2017, annual global material extraction tripled continuing to grow and pose serious risks worldwide. About half of the total greenhouse gas emissions and over 90% of the biodiversity loss and water shortage are due to resource extraction and processing of materials, fuels and food. The EU industry has begun to change but it still accounts for 20% of the EU greenhouse gas emissions. It remains too “linear” and depends on the amount of new materials that are extracted, traded and processed into goods and eventually disposed as a waste material or emissions. Of the materials EU uses, only 12% are recycled (European commission, 2020).

To manage the climate change, the EU has already pursued a new policy. It is completely adapted to the climate change strategy that was announced in 1992. It was endorsed for the treaty on climate change aiming to limit the global warming to well below 2 degrees Celsius above the pre-industrial levels of the continent. In 2001 the EU succeeded in strengthening its values and becoming an international leader in terms of climate change when it was supported enough by the followers of the Kyoto protocol.

Furthermore, some ambitious policies backed up the European Union’s role in the world (Siddi, 2020).

Figure 1 traces the dynamic development of sustainability strategies of the European Commission.

The European Green Pact provides an action plan aiming to increase resource efficiency by moving to a clean, circular economy, restoring biodiversity and reducing pollution. The plan specifies the necessary investments and the available financial instruments. It explains how to ensure a fair and united transition of economy.

The EU aims to be climate neutral in 2050. European Climate Law has been proposed to make this political commitment a legal obligation. Achieving this goal will require action by all sectors of the EU economy, such as: investing in green technologies, supporting industrial innovation, introducing cleaner, cheaper and healthier forms of private and public transport, decarbonising the energy sector, improving the energy efficiency of buildings and working with international partners to improve environmental standards worldwide (Sikora, 2021).
Attitude of the European Green Pact towards the mineral resources industry

The raw material industry plays a central role in achieving sustainable development. The new European Green Deal is addressing all policy areas relevant to sustainable mining management: climate change, biodiversity, agriculture and desertification, including sustainable water management. Human wellbeing is necessarily at the core of the European policies. The industry will be in the focus of the green policies and at the same time, it will be the major challenge in front of us in the next years.

There is no doubt that the EU has taken this step to make the whole of Europe green and free of carbon. The current situation of the member-countries has predisposed a lot of opportunities in this way. The outbreak of COVID-19 and the climate crisis have already led the countries to think about the positive factor of the carbon elimination that will influence health and environment. The green transition to new technologies like renewable energy, stationary energy storage and e-mobility is dependent on the critical raw materials that include neodymium, cobalt, tungsten, niobium, tantalum, etc. (Claeys, 2019).

There are a lot of challenges in the way of the Green Deal implementation when it comes to raw mineral industry. Currently, the environmental and social impacts of extracting and processing resources from the earth are very high.

National Recovery and Sustainability Plan

The European Recovery and Resilience Facility will make 672.5 billion EUR of loans and grants available to support reforms and investments by Member States. To access the funds, each Member State shall create a National Recovery and Resilience Plan, covering the period 2021-2026, and drafted in cooperation with its regions (European Commission, 2021).

The green transition is at the forefront of the Bulgarian Recovery and Sustainability Plan, concentrating almost half (47%) of the total projected costs. In this way, the country will contribute to the implementation of the Pan-European targets for gradual decarbonisation. In addition, efforts are focused on three main areas: (i) creating conditions for the accelerated introduction of renewable energy sources and hydrogen; (ii) enhanced actions to increase the energy efficiency of the economy; (iii) sustainable mobility (National Recovery and Resilience Plan of the Republic of Bulgaria, v. 1.2, 2021).

The ultimate objective of the Recovery and Resilience Plan is to facilitate economic and social recovery from the crisis caused by the COVID-19 pandemic so that the Member States are prepared for the green transition. In pursuit of this goal, the European Commission has grouped a set of measures and reforms that will not only restore the potential for economic growth but will also develop it by ensuring the resilience to negative external factors. This will allow, in the long run, achieving the strategic goal of the Commission for convergence of the economy and incomes to the EU-average ones. At the same time, the Plan lays the foundations for a green and digital transformation of the economy, in the context of the ambitious goals of the Green Deal.

The plans should give particular focus to answering challenges identified in the European Semester and contributing to sustainable growth. Indeed, every recovery and resilience plan must have a minimum of 37% expenditure related to green investments and reforms, supporting implementation of the European Green Deal (Interreg Europe, 2021).

The renewables, besides demonstrating the growth capacity, have become a very important energy source for industry.

Figure 2 illustrates a RMI’s (Rocky Mountain Institute) study which presents renewables on mine sites, with cumulative commissioned capacity surpassing 1.7 GW, far beyond the 1.4 GW goal set for 2022 (Kirk and Cannon, 2020).
EU energy governance and the Green Deal from the perspective of the mining industry

Several innovative exploration techniques have been developed by projects of Horizon 2020 to find minerals and ores which can make Europe a climate-neutral continent. Thus, Europe will be with a better economy and sustainable energy resources. According to 6 of the highlighted cutting-edge projects of the EU, access to resources is one of the most essential and complicated questions in terms of the Green Deal accomplishment since its main aim is to make Europe a carbon-neutral continent by 2050 (Brodny, Tutak, 2020).

Moreover, the Commission has set a plan to raise the EU’s ambition on reducing greenhouse gas emissions to 55% below the levels of 1990 by 2030. Defence sectors, mobility, renewable energy production, electric vehicles, mobile phones and other means that are taking part in the consumption of energy will be made carbon neutral by 2050 (CORDIS, 2021).

The transition of energy is defined by the International Renewable Energy Agency. It is a pathway for the world to enhance the global energy sector by decreasing the usage of fossil-based fuels to zero percent by the mid of this century. It is very obvious that the role of mining and usage of coal is very essential to overcome the energy demand but at the same time it causes the need for global energy transitions because of the warming effect around the whole world.

During the past few decades, the transitioning to low-carbon systems of energy has been underway. As a consequence, the renewable energy brings 72% of new global power capacity in 2019 (www.renewablesnow.com). At present it is expanding being a strategic tool of the regulations of the governments of most EU countries. Other factors that help the development of the renewable energy sector are outcomes from the Paris agreement where incentives and other encouragements were set to make citizens more active in meeting the decarbonisation and goals of zero-carbon climate. Some other countries in the EU have transitioned the support schemes of the past into auctions to purchase power through agreements.

Figure 3 illustrates all 17 minerals, which are used for different applications in the energy sector. The analysis of World Bank compares the mineral demand coming from the 10 energy technologies under the 2-degree scenario of temperature rise (2DS) and compares it with 2018 production figures. Panel a provides the percentage increase in mineral demand based on 2018 production figures with the majority of demand coming from the minerals needed for batteries, specifically graphite, lithium and cobalt. These minerals will be needed at scales significantly beyond current production levels, by up to as much as five times. Panel b presents the annual absolute increase in mineral production up to 2050, with production figures being the highest for aluminium, graphite, and nickel. Graphite demand increases in both absolute and percentage terms since graphite is needed to build the anodes found in the most commonly deployed automotive, grid, and decentralised batteries. About 4.5 million tons of graphite is needed to be produced annually by 2050, or a cumulative of 68 million tons, while graphite demand increases by nearly 500 percent from 2018 production figures, demonstrating the critical role graphite plays in the clean energy transition, being used in Li-ion batteries, the most widely projected deployed battery technology (Hund, Porta, Fabregas, Laing, Drexhage, 2020).

Wind, thermal and especially photovoltaic technologies are more suitable for the Green Deal commitment of the EU. Illustrated by numbers of the specific renewable energy technology, it means that the power capacity of 1 MW is equal to 3000 solar panels production. In the scenario of electric transportation and wind power, each turbine contains almost 3.5

Fig. 3. (a) Annual demand from energy technologies as percentage of 2018 production, (b) Annual demand from energy technologies in 2050, in million tonnes (Hund, Porta, Fabregas, Laing, Drexhage, 2020)
tons of metal in the form of stainless steel, iron, copper, etc. About 83 kg of copper is required in an electric vehicle. In this way, the overall demand for niche and base minerals, originating from the clean energy technology manufacturing, will grow significantly. In particular, the expected increase in the consumption of metals such as graphite, lithium, cobalt, etc. will need to be significantly ramped up by more than 450 % by 2050 from 2018 levels - to meet demand from energy storage technologies (Hund, Porta, Fabregas, Laing, Dreuxhage, 2020).

The prospects of demands suggest some promising opportunities in resource-rich countries, prompting governments of different countries. One of them is Bolivia having ¼ of the worlds’ resources of lithium. The Democratic Republic of Congo and Chile are taking in policy and investment options for support and development of mining industries that are highly considered in the global energy transition context (Siddi, 2020).

With the increased demand for materials, the research and innovation led by the European Union are funded under the largest ever European funding programme Horizon 2020. Exploration of minerals is usually conducted in search of rich ores that could be used in the industries and for commercial purposes. At the moment it is very complicated to estimate the availability of resources in the core of the earth due to the severity of mining operations (Jones, 2021).

The overall expenses of energy are to be estimated at approximately 30% of the total cash operating costs of companies operating in the mining industry. The percentage of consumed energy is about 32% in the form of electricity. It is to be noted that the financial aspect is usually a more considerable motive for most of the companies and together with the decreasing costs of renewable energy in the last decade, the integration of renewable technologies and sources in mining has been a considered and performed process in the past few years (Eurostat, 2021).

For a few years, the renewable energy has been the chosen power supply in cases where the cost of electricity is highly significant. It was mostly applicable for the case of mining in remote areas where the electricity cost from the grid are more substantial, as well as places suffering energy disruptions (Claeys, 2019).

Due to the change in climate conditions and the momentum of the industry and sources of renewable energy gaining awareness in the world, they have become more cost competitive than ever before. Different mining companies in the EU are expanding the share and interests in renewable energy sources for powering their operations in specific countries.

This is possible through agreements for power purchasing or joint ventures with companies providing power by purchasing certificates of renewable energy or by the mining company’s own micro grid. Undoubtedly, the assessment made by different projects show that there is still a long way to 100% renewable energy projects in the EU. Some experts say that hybrid solutions are somehow very much competitive, providing 50% of the energy from renewables.

It is considered that the global greenhouse effect due to mining is about 4-7%.

The change in climate conditions is a threat also to the mining sector. Therefore, different countries of the EU have already started thinking about a way to stop it (Brodny, Tušak, 2020). Mining industry has never ignored its responsibility of taking care of the environment. The technology advancement has already led industries and various power generation companies to automation which ensures less human involvement. Furthermore, hazardous operations are usually done through robots and computer applications. However, drilling and exploration use equipment for locating and extracting minerals and that requires a very precise approach, human interference and actual implementation.

Advancements in renewable energy technologies and the industry commitment are a precondition for some benefits to renewable energy companies and the mining sector. These are: less reliance on carbon-related fuels, vulnerable fluctuations of global pricing, reduction in carbon emissions and specific ones from mines that consume a huge amount of electricity.

Environmental satisfaction and social criteria are used for the measurement and sustainability of green credentials of the specific projects. Improved engagement of investors will shift the debt of the capital market to green and sustainable markets that comply with the SDG and ESG indicators.

The situation for Bulgaria

The Bulgarian economy is one of the most resource-intensive in the EU, lagging behind the Member States of the Community in terms of applying the principle of circular economy and implementing eco-innovation activities. The economy spends on average 3.5 times more energy resources per unit of GDP than the average energy consumption in the EU.

In the industry sector there is no significant improvement in energy efficiency. The reasons for this include the lack of significant changes in the industrial structure, as well as a significant improvement in terms of technologies used and production processes. As a result, the energy intensity of Bulgarian industry remains the highest in the EU, almost three times higher than the EU average. To a large extent, the same applies to the services’ sector, where, however, the gap with the EU is smaller (2.5 times). Figure 4 illustrates the share of energy from renewable source in 2015 in % gross final energy consumption. Note the position of the Bulgaria as one of the better countries in the European class (Eurostat, 2021).

Bulgaria remains the most carbon-intensive EU Member State, as the intensity of greenhouse gas emissions in the Bulgarian economy is more than 4 times higher than the EU average with a positive but modest trend of shortening the gap in this regard in recent years. The energy sector is the largest source of greenhouse gas emissions in the country with over 70% of the total emissions in the country. Coal-fired thermal power plants account for almost half of the sector’s emissions but do not have access to adequate infrastructure to allow them to change their fuel base.

The desire to decarbonise the economy necessitates large-scale reform of the energy sector in the country which in turn is associated with significant investment needs for phased replacement of fuel in power plants through the use of alternative environment friendly energy sources.

The EU’s goal is to create opportunities to phase out the use of coal for electricity generation and to gradually replace the fuel...
base in thermal power plants in the country’s coal regions through the use of alternative environment friendly energy sources. This will lead to a reduction and subsequent elimination of greenhouse gas emissions resulting from the production of electricity from solid fuels in these regions.

Conclusions

The agreement and the plan of the EU countries to lower the carbon emissions till 2050 can pose a challenge to the power sector requiring improvements to be made focused on the climate change. More or less, the processes related to the extraction of minerals and metals will be unavoidably explored also by the renewable energy technologies. The aim is to achieve a prominent change in the greenhouse effect in the EU. Except the geothermal energy, the production of hydro, wind and solar energy are well developed. District heating through geothermal energy, biomass and waste can and should be developed.

Unfortunately, Bulgaria lags behind the goals of the European Green Deal, but there is the potential for rapid progress. We have unique advantages that we could use, the funding for which we could receive via the Impact and Sustainability Plan.

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OPTIMISATION OF THE PARAMETERS OF CYCLICAL-STREAMING TECHNOLOGY IN THE CONDITIONS OF THE DEVELOPMENT OF KRYVBAS IRON ORE DEPOSITS

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ABSTRACT. The state of open-pit mining, formed at Ukrainian enterprises, as well as the state of the mineral raw materials market require the search for new, more economically feasible approaches to open pit mining operations. Such a solution is the widespread use of cyclical-streaming technology. The aim of the paper is to research the interconnection between the main technological parameters of cyclical-streaming technology. In the paper relationships are established and the rational values of the parameters of the cyclical-streaming technology are determined, which contributes to improving the economic indicators of deposit development.

The mathematical modelling of the main parameters of the cyclical-streaming technology is fulfilled. The obtained results of studies of the main parameters of the cyclical-streaming technology can be used by project organisations and mining enterprises in the design.

The comparison of optimal indicators of operation of the excavator-automobile complex and cyclical-streaming technology is performed, as a result of which the economic expediency of the latter was confirmed. It has been established that increasing the carrying capacity of more than 136 tons at the current level of development of machinery and technology in iron ore open-pits in most cases is not appropriate. At the same time, the influence of the efficiency of the excavator unit on the performance of the cyclical-streaming technology in general was investigated. As a result, it was established that the best technical and economic indicators will be reached using the EKG-10 excavator. In this case, the geometric capacity of the dump truck body must correspond to the capacity of the bucket, and the load capacity is up to 130 tons. Thus, the study confirms the technological parameters of the cyclical-streaming technology that have been developed in the open-pits of the mining and processing plants of Kryvbas region.

Key words: the cyclical-streaming technology, excavator-automobile complex, equipment performance

The problem and its connection with scientific and practical tasks

Further development of opencast mining will be characterised by a gradual deterioration of mining conditions of deposit development. At the same time, the current state of Kryvbas open pits is characterised by their considerable depth and their further growth to the design marks. However, the increase in depth is accompanied by an increase in the volume of overburden, that is removed from the open-pit and this increases the load on the system of transportation of rock mass. Mining conditions for the development of mineral deposits in the coming years will be characterised by a further increase in the depth of open-pits and transportation distances, increasing the part of strong rocks and ores in total rock mass, as well as the need for selective development and averaging of ores while concentrating on lower horizons and in cramped conditions.

All this requires the use of several, mostly combined, modes of transport in the development of deposits, in combination with the existing quarry excavation equipment – cyclical-streaming technology (CST). If in the past the question of application of CST was raised, today's mining and technical-economic conditions demand search and the reasonable choice of the most rational parameters of cyclical-streaming technology, especially: working parameters and standard size of the excavating equipment, automobile and conveyor transport, parameters of elements of the development system, etc.

Analysis of research and publications

In recent years, the depth of the iron ore open-pits of Kryvbas («Central MPP», «Pivnichny MPP», «Inguletskiy MPP», «AMKRo») has been increased by 100-150 m and is currently 300-450 m. For example, the depth of «Arcelor Mittal Kryvyi Rih» open-pit № 2b is 300 m, open-pit №3 is 375 m, «Inguletskiy MPP» is 450 m, «Central MPP», open-pit №1 is 400 m, open-pit №3 is 315 m, «Pivnichny MPP» Gannikovshy open-pit is 350 m). In the future, in accordance with the completed technical projects, the development depth will increase to 500-700 m (Chetverik et al., 2010, 2012, 2014; Bass, 2017). At such depths, the problems of rock mass transportation due to excessively long transportation distances become even more complicated. Currently, the widespread is the use of road delivery of rocks and minerals by heavy-duty dump trucks, the flexibility of which is still its main advantage over other modes of transportation. However, the constant increase in the cost of diesel fuel, tyres, lubricants, which account for up to 90% of operating costs for road delivery of rock mass necessitates the use of a more economical method of transporting minerals and rocks to the surface – a conveyor in combination with road transport in a quarry, i.e. CST.

The feasibility of using CST is justified primarily by a significant reduction in operating costs compared to variants that involve the use of an open-pit road or rail transport. Thus, according to foreign practice, the use of crushing complexes in the open-pit and conveyor transport significantly reduces operating costs compared to the transportation of ore by dump trucks. This creates favourable conditions for more efficient mining and reducing the amount of exhaust gases. However, one of the disadvantages of the applied CST schemes is the permanent position of crushing and conveyor complexes, the use of which does not correspond to the dynamics of mining operations and the conditions of formation of technological cargo flows.

Although CST is cheaper than road transport, with increasing depth of open-pits, its use with a stationary crushing and reloading points becomes less profitable.

According to (Yakovlev, 2003; Rakishev, 2012), the permanent position of crushing and conveyor complexes...
facilities and the irrationality of the mining schemes used in such cases result in a large amount of mining capital and installation works (up to 75% of the total cost of the complexes).

The placement of crushing and reloading points require a large working berm of significant size, which for it is necessary to perform additional volumes of excavation work (from 2 million m³ for a depth of 100 m to 10 million m³ of rock mass at a depth of 500 m).

Large volumes of mining and capital works result in longer construction times of crushing and conveyor complexes which take, as a rule, not less than 3-5 years (Karmayev, 2012; Trubitskoy et al. 2015).

The development of a scientific basis of the cyclical-streaming technology can be divided into several stages (Reshetnyak, 2015).

Depending on the size of the open-pit, the use of the CST complex at the first stage allows to reduce the volume of current overburden to an average of 5 million m³. At the same time at CPT with a steeply inclined conveyor the volumes of mining and capital works decrease 3-4.5 times, expenses of diesel fuel are reduced 1.8-2.5 times, dust emission and emissions of toxic components in the atmosphere decrease by 35-45%.

The next stage in the development of a cyclical-streaming technology was the creation and implementation in the open-pits of mobile crushing and reloading points, equipped with steeply inclined conveyors designed to lift the rock mass to higher benches (Sheremetov, 2007). The structure of such a complex includes a hopper, feeder, crusher and a steeply inclined belt conveyor (type "sandwich") with a clamping belt. Another feature of this crushing and reloading point is the installation of a compact and high-performance auger crusher instead of the traditional jaw or conical one. The use of such a loader with a capacity of 2000 m³/h at the Muruntau open-pit (Uzbekistan) allowed to reduce the distance of rock mass transportation by road by 480 m and the lifting height by 60 m (Yakovlev, 2003).

According to Muruntau open-pit experts (Kucherskiy et al., 2005), the advantages of CST based on steeply inclined conveyors are not only the reduction in the cost of transportation of rock mass, but also the significant reduction in preparatory work because the conveyors can be placed on a narrow strip of the reconstructed section of the open-pit board practically without additional capital trenches and penetration of inclined trunks. However, as the analysis shows, at this time the part of rock mass removed from open-pits by CST in the CIS countries is still very small (only 10-15%), while in the enterprises of Canada, USA, Chile, Australia, it exceeds 50% of total mineral production (Chetverik et al., 2010). Therefore, in order to significantly improve the economic performance of large mining companies, as well as to reduce the negative impact of mining on the environment, it is advisable to significantly expand the use of cyclical-streaming technology in these enterprises.

**Formulation of the problem**

Based on the analysis of scientific advances on the use cyclical-streaming technology in the open-cast development of deposits, there is a need to establish mathematical dependences and rational values of the parameters of CST.

**Presentation of material and results**

The main link, the crushing and conveyor complex (CCC), through which the supply of ore to the CCC is stopped, is characterised by the following downtimes. The duration of maintenance and scheduled repairs of equipment, carried out in accordance with the standards for repair schedules, reaches 7.5 – 10.5% of the calendar time. Downtime of the complex for technological and organisational reasons with the number of stops of up to 80 – 140 is 35 – 74 hours per month. Due to emergency reasons, CCC stand for 48 – 78 hours with the number of stops 90 – 140 during the month. It follows that each complex during the year stops about 1000 – 1680 times, briefly changing the state of the transport system due to a decrease in its productivity at such intervals. The average decrease in system productivity due to stops of the crushing-conveyor complex in some months is 4.6 - 6.2%. However, it is obvious that most of the downtime of the crushing complex is due to emergency stops as a result of equipment failure. The solution to this issue is beyond the scope of this research.

Irregular operation of gathering vehicles leads to a decrease in the productivity of the crushing and conveyor complex and excavator unit. The overall decrease in the average variable productivity of the CST system due to the lack of dump trucks in some months varies in the range of 1.6 - 3.7%. For the crushing and conveyor complex and excavator link, this indicator is 0.2 - 2.3% and 0.8 - 1.8%, respectively. In certain periods of time to perform the planned tasks, crushing and conveyor systems are serviced by dump trucks, which quantitatively exceed the number required to ensure average hourly productivity. This reserve of gathering equipment, as usually, is suboptimal and practically does not give the required increase in hourly cargo flow. Such measures increase the overall unevenness of cargo flows, violating the modes of excavation of other types of rock mass in the open-pit.

For example, due to the fact that for the maintenance of the crushing and conveyor complex "hor. - 195 m" in the Pershotravneviy open-pit of «Pivinchniy MPP» in one of the years of its stable operation were spent 10% more track-hours than the required level, the volume of removal of overburden from the open-pit decreased by 7%.

Thus, one of the main parameters of the CST is the production capacity of the transport link. To study this question, we turn to the paper of Suprun and co-authors (2014). Figure 1 shows the results of research conducted by "Caterpillar" and "Komatsu" on behalf of JSC "Chernihivets", namely the dependence of the cost of removal of 1 tkm on the load capacity of the dump truck.

It is obvious that with increasing the load capacity, the transportation costs decrease. However, the intensive reduction occurs only in zone A (Figure 1) with an increase in load capacity from 40 to 130 tons, and further reduction is quite insignificant. But the carrying capacity of dump trucks used in domestic open-pits has already reached zone B of this schedule, so its further increase is impractical without good technological reasons.

According to Table 1, the internal shifts of a simple excavator unit for technological and organisational reasons reached 825 hours per month.
faces, cleaning oversized pieces of rock mass, cleaning of faces and horizons), busy by moving to a new place of work or from the blasting zone or stand idle due to lack of dump trucks.

Downtime of excavators due to equipment failures is 2-2.5 times less than the downtime for technological and organisational reasons. The average decrease in productivity of CST complexes due to downtime of excavators during different months varies between 8.7 - 14.7%, which is about 50 - 65% of the total average decrease in productivity of the system of cyclical-streaming technology.

Therefore, we will investigate the interdependence of excavator bucket capacity, excavator productivity and utilisation ratio on the efficiency of the system of cyclical-streaming technology.

To do this, we calculate the productivity of excavators EKG-4.6, EKG-5, EKG-8I, EKG-10, EKG-12.5, EKG-15 and EKG-20 for different utilisation ratios and for each value set the specific costs. The results of such calculations for the utilisation ratio \( k_v = 0.55 \) are given in Table. 2.

Similarly, the values of the reduced costs were obtained for \( k_v=0.5, k_v=0.65, k_v=0.7 \) (Table 3). According to the obtained data for \( k_v=0.55, k_v=0.6, k_v=0.65, k_v=0.7 \), the dependences of the reduced costs on the productivity of excavators were constructed, they are shown in Figure 2.

Table 1. Reduction of production capacity of the complex of cyclical-streaming technology due to technological downtime of adjacent units

<table>
<thead>
<tr>
<th>Technological link of the CST system</th>
<th>The share of reduction of average variable production capacity by months</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Excavator</td>
<td>0.51</td>
</tr>
<tr>
<td>Road gathering</td>
<td>0.1</td>
</tr>
<tr>
<td>Crushing and conveyor complexes</td>
<td>0.33</td>
</tr>
<tr>
<td>Crushing and concentrating factory</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Table 2. Calculation of excavator productivity and reduced costs for \( k_v=0.55 \)

<table>
<thead>
<tr>
<th>Excavator</th>
<th>Bucket capacity, m(^3)</th>
<th>( k_v )</th>
<th>Productivity, m(^3)/year</th>
<th>CAPEX, c.un./year</th>
<th>OPEX, c.un./year</th>
<th>Reduced costs, c.un./year</th>
</tr>
</thead>
<tbody>
<tr>
<td>EKG-4.6</td>
<td>4.6</td>
<td>0.55</td>
<td>1785818.57</td>
<td>74883.31</td>
<td>1499142.9</td>
<td>1510375</td>
</tr>
<tr>
<td>EKG-5</td>
<td>5</td>
<td>0.55</td>
<td>1863462.86</td>
<td>79630.057</td>
<td>1500487.1</td>
<td>1512432</td>
</tr>
<tr>
<td>EKG-8I</td>
<td>8</td>
<td>0.55</td>
<td>2329328.57</td>
<td>112598.83</td>
<td>3106003.9</td>
<td>3122894</td>
</tr>
<tr>
<td>EKG-10</td>
<td>10</td>
<td>0.55</td>
<td>2451924.81</td>
<td>132729.13</td>
<td>4767003.1</td>
<td>4786912</td>
</tr>
<tr>
<td>EKG-12.5</td>
<td>12.5</td>
<td>0.55</td>
<td>2773010.2</td>
<td>156458.3</td>
<td>5956079.6</td>
<td>5979548</td>
</tr>
<tr>
<td>EKG-15</td>
<td>15</td>
<td>0.55</td>
<td>2911660.71</td>
<td>179962.94</td>
<td>7440398.6</td>
<td>7467243</td>
</tr>
<tr>
<td>EKG-20</td>
<td>20</td>
<td>0.55</td>
<td>3583582.42</td>
<td>221235.82</td>
<td>9521495.3</td>
<td>9554681</td>
</tr>
</tbody>
</table>
The graph shows that with increasing productivity, the costs are reduced. But at the same time, the lowest costs are characteristic of larger values of the utilisation factor.

Therefore, when substantiating the productivity of the excavator link, it is necessary to take into account the conditions of use of loading and unloading equipment, as well as the current state of transport communications, which determine the possibility of using more powerful transport equipment.

However, these calculations are theoretical. In fact, based on the experience of MPP, higher utilisation ratio is typical for excavators of smaller sizes. Therefore, in Table 4 the dependences of the reduced costs on the productivity of excavators during their operation with the corresponding empirical coefficients of equipment use are summarised, and in Figure 3 these data are visualised by the range of values and given a correlation line that can be described by the equation $y = 6 \times 10^6 x^2 + 3.6685x - 10^7$. The correlation ratio was $R^2 = 0.8455$.

### Table 3. Calculation of excavator productivity and reduced costs for $k_v=0.6$, $k_v=0.65$, and $k_v=0.7$

<table>
<thead>
<tr>
<th>Excavator</th>
<th>Productivity, $m^3$/year</th>
<th>Reduced costs, c.un./year</th>
<th>CAPEX, c.un./year</th>
<th>OPEX, c.un./year</th>
<th>Reduced costs, c.un./year</th>
</tr>
</thead>
<tbody>
<tr>
<td>EKG -4.6</td>
<td>1948165.714 / 1646661</td>
<td>2110512.86 / 1782947</td>
<td>2272860 / 1919233</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EKG -5</td>
<td>2032868.571 / 1648839</td>
<td>2202747.29 / 1785247</td>
<td>2371680 / 1921655</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EKG -8I</td>
<td>2541085.714 / 3405258</td>
<td>2752842.86 / 3687622</td>
<td>2964600 / 3969986</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EKG -10</td>
<td>2674827.068 / 5220276</td>
<td>2897729.32 / 5653640</td>
<td>3120631.58 / 3969986</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EKG -12.5</td>
<td>3025102.041 / 6521010</td>
<td>3277193.88 / 7062472</td>
<td>3529285.71 / 7603934</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EKG -15</td>
<td>3176357.143 / 8143643</td>
<td>3441053.57 / 8820043</td>
<td>3705750 / 9496443</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EKG -20</td>
<td>3909362.637 / 10420271</td>
<td>4235142.86 / 11285862</td>
<td>4560923.08 / 12151452</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 4. Calculation of excavator productivity and reduced costs for empirical values $k_v$

<table>
<thead>
<tr>
<th>Excavator</th>
<th>$k_v$</th>
<th>Productivity, $m^3$/year</th>
<th>CAPEX, c.un./year</th>
<th>OPEX, c.un./year</th>
<th>Reduced costs, c.un./year</th>
</tr>
</thead>
<tbody>
<tr>
<td>EKG -4.6</td>
<td>0.8</td>
<td>2597554.286</td>
<td>74883.3102</td>
<td>2180571.498</td>
<td>2191803.995</td>
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<tr>
<td>EKG -5</td>
<td>0.78</td>
<td>2642729.143</td>
<td>79630.05698</td>
<td>2127963.485</td>
<td>2139907.993</td>
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<tr>
<td>EKG -8I</td>
<td>0.75</td>
<td>3176357.143</td>
<td>112598.8269</td>
<td>4235459.8</td>
<td>4252349.624</td>
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<td>EKG -10</td>
<td>0.7</td>
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<td>132729.1265</td>
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</tr>
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<td>EKG -12.5</td>
<td>0.65</td>
<td>3277193.878</td>
<td>156458.2999</td>
<td>7039003.184</td>
<td>7062471.929</td>
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<tr>
<td>EKG -15</td>
<td>0.6</td>
<td>3176357.143</td>
<td>178962.939</td>
<td>8116798.43</td>
<td>8143642.871</td>
</tr>
<tr>
<td>EKG -20</td>
<td>0.55</td>
<td>3583582.418</td>
<td>221235.8209</td>
<td>9521495.279</td>
<td>9554680.652</td>
</tr>
</tbody>
</table>
At the same time the larger number of smaller excavators promote more equitable development of mining operations on the ledges and reduce process downtime.

![Fig. 3. Dependence of the reduced expenses on productivity of excavators for empirical values k,](image)

Table 4 shows that with increasing the size of the excavators, the utilisation ratio of the equipment decreases over time (in each case, a dump truck with a capacity of 130 tons is used). This is explained by the fact that for the use of more powerful dump trucks it is necessary to increase the width of the road and, accordingly, the width of the working area, which will reduce the angle of the working board and, accordingly, worsen the mining regime.

At the same time, the capacity of the excavator bucket should correspond to the load capacity of the dump truck, which, in turn, is recommended to be within 130 tons. Today, with the current level of development of equipment and technology, such a combination will provide the highest technical and economic performance of opencast mining. At the same time, the experience of domestic iron ore open-pits confirms the research data.

Conclusions and directions of further research

The paper discusses in detail the interconnection between the parameters of CST. The reduced costs of transportation, the number of dump trucks and the productivity of the excavator-automobile complex in the CST and their dependence on the depth of deposit development are analysed. Particular attention is paid to the comparison of the optimal productivity of the excavator-automobile complex and cyclical-streaming technology, which confirms the economic feasibility of the last one. It is found that increasing the carrying capacity to more than 136 tons at the current level of development of machinery and technology in iron ore open-pits in most cases is not appropriate. At the same time, the influence of the efficiency of the excavator link on the productivity of the CST as a whole is investigated according to the criterion of minimum equipment downtime.

As a result, considering the current state of open-cast mining it is found that for the conditions of iron ore open-pits of Kryvyi Rih the best technical and economic indicators will be achieved when using excavators with a bucket capacity of 10 - 12.5 m³. Thus, the research confirms the technological parameters of cyclical-streaming technology that have been developed in the open-pits of mining and processing plants.

References

ABSTRACT. One of the many environmental problems resulting from electricity generation in thermal power plants is the release of large amounts of solid wastes (coal combustion products). In the absence of effective eco-friendly disposal practices, this waste is accumulated in the form of coal ash embankments or in the excavated parts of the open-cast mines. The so constituted big landfills and surface impoundments emit leachate emissions containing a wide range of conventional pollutants among which, by definition, sulphate ions (SO_4^{2-}) dominate. Using the computer program VS2D, a numerical model is developed of the conditions for mass transport of pollutants (using the example of SO_4^{2-}) from the designed new embankments for deposition of non-hazardous industrial solid waste from TPP in the area of the internal embankments of Troyanovo-North open-cast mine, part of the Maritsa East Coal Mining Complex. The scheme of convective-diffusion mass transport is employed, taking into account reversible elimination (sorption-desorption), mechanical dispersion and mixing. On the basis of the developed model, a long-term prognosis (100 years) is made for the extent and the degree of subsurface contamination from the new embankments. Based on the model solutions, the retention capacity of the geological foundation and the risk of groundwater pollution are assessed.

Keywords: environment protection, mass transport models, groundwater and soil contamination, landfills for solid waste from TPP, Maritsa East Coal Mining Complex.

Introduction

Despite their negative global impact on climate, environment and humans, fossil fuels (oil, gas and coal) still account for about 85% of the world energy sources, with only the share of coal being about 27% (BP statistical review of world energy, 2019). As a result, substantial amounts of extremely harmful carbon-containing containing waste gases, aerosols, liquid emissions and solid compounds are released into nature, which are the reason for air, water and soil contamination.

One of the largest sources of pollution worldwide is the generation of electricity in thermal power plants. Studies show that in addition to the notorious problem of air pollution related to this type of electricity generation, another serious challenge is the release of large amounts of residual products from coal combustion plants (CCPs).

Globally, the total volume of CCPs produced per year is about 1222 Mt, with China having the largest share - 565 Mt, India - 197 Mt and the United States - 107.4 Mt (Harris et al., 2020). At the same time, all European countries emit about 140 Mt per year, with the main share (about 100 Mt) falling on non-EU countries and Eastern European countries which joined the EU after 2004. Currently, the overall recycling rate of all CCPs is about 64%, with Japan leading the way - 99.3%, the EU15 - 94.3%, Israel - 90.9% and Korea - 85.4% (Harris et al., 2020). Unfortunately, the problem of CCPs still does not find good solutions in many Eastern European countries and in those outside the EU15.

The CCPs released during the generation of electricity in thermal power plants in coal mining complexes are usually deposited in the form of coal ash embankments or in the excavated parts of the open-cast mines. The leachate emissions produced by these landfills contain a wide range of conventional and priority pollutants, including B, SO_4^{2-}, Br, F, Cl, K, Na, Ca, As, Ba, Be, Cd, Cr, Co, Hg, Li, Mo, Pb, Sb, Se, Ti, and Ra^{226/228} (USEPA, 2009; EPRI, 2012, 2015; Hensel, 2016). When assessing the impact of CCPs on groundwater and soil, as principally typical and relatively highly mobile contaminants that enter the subsurface are regarded B, Mo, Li, SO_4^{2-}, Br, F, Cl, K, Na, and Ca, and as most indicative amongst them are recognised B and SO_4^{2-} (EPRI, 2012; Rocha et al., 2017).

In Bulgaria, the main source of electricity generated in thermal power plants is the Maritsa East Coal Mining Complex, which is the largest one in South-eastern Europe. The coal mining complex includes several open-cast lignite mines – Troyanovo-1 Mine, Troyanovo-3 Mine, Troyanovo-North Mine, which supply coal to the large power plants built at the complex TPP AES Galabovo, TPP Maritsa East 2 and TPP Maritsa East 3. The CCPs produced by these coal-fired thermoelectric power-production facilities are accumulated in the form of coal ash embankments built in the complex or in the excavated parts of the open-cast mines. The lignite used in electricity generation is characterised by extremely low calorific value, high ash content and very high sulphur content. This fact presupposes that the three thermal power plants emit huge amounts of solid residue not only from coal combustion, but also from flue gas desulphurisation facilities. Studies show that the consequences are severe and some problems, generating critical environmental issues, are present in the area of the coal mining complex, affecting all elements of the environment and human activity (Zheleva et al., 2004; Nikolova et al., 2010; Petrov, 2019).

The main task of the performed model studies is to achieve a quantitative prognosis for the extent and degree of possible subsurface contamination caused by liquid emissions incoming from the designed new embankments for deposition of CCPs from TPP AES Galabovo in the area of the internal embankments of Troyanovo-North Mine (Figure 1). According to the proposed approach, a two-dimensional (2D) numerical model of the conditions for mass transport of pollutants is developed, following the example of highly mobile sulphate ions (SO_4^{2-}). One extremely severe assumption for a continuous inflow of pollutants from the new embankments over a period of 100 years is accepted in the model.

Based on the obtained model solutions, the retention capacity of the geological basement and the potential risk of groundwater pollution have been determined.
Methodological approach

The proposed methodological approach for predicting the possible spread and intensity of subsurface contamination caused by the embankments for deposition of CCPs implicate the use of two-dimensional computer models of fate and transport of pollutants in a variably saturated porous media. The development of these models is based on the following assumptions and general schemes for simulating the source of contamination, the studied part of the near-surface section, the processes of mass transport and the form of the model solutions:

(i) The conditions for mass transport of highly mobile pollutants are simulated on the example of SO₄, which is considered as a key pollutant. The main reasons for this choice are: (a) this pollutant is among the most indicative ones when tracing CCPs leachate (EPRI, 2012); (b) it is conservative, moves at a pace comparable to the infiltration rate and marks the maximum spread of possible contamination in the subsurface area; (c) sulphate ions are easily soluble and have a high concentration in the new embankments.

(ii) The subsurface area is reconstructed with the specific parameters of the hydrogeological units established in the near-surface section: geometric parameters – top and bottom layers z = f(x), average thickness m; physical properties – density ρ, porosity n; hydrodynamic properties – saturated hydraulic conductivity k, saturated water content θₛ, residual water contentθₑ, unsaturated hydraulic conductivity function (relative hydraulic conductivity) kᵣ; hydraulic characteristic functions – relations between pressure head h, moisture content θ and relative hydraulic conductivity kᵣ; mass transport parameters – distribution coefficient of the key pollutant KᵣSO₄, dispersivity α, molecular diffusion Dᵣm, coefficient of irreversible elimination y.

(iii) The groundwater recharge by infiltration and percolation is set in accordance with the specific climatic, soil and technogenic conditions.

(iv) The mechanism of the mass transport of pollutants is in its full form: convective transport accompanied by reversible elimination (adsorption and ion exchange), irreversible elimination (precipitation or decay), mechanical dispersion (longitudinal and transverse), molecular diffusion and mixing.

(v) The potential surface contaminator simulated in the mathematical models is set as a line source of pollution. The concentration of SO₄ in the CCPs leachate is set as a constant value for the entire period of the simulation CᵣSO₄ = const.

(vi) In order to simplify the model, the following reasonably conservative assumptions are also accepted: the infiltration rate is constant over the entire model area, and the concentration of SO₄ is homogeneously distributed along the entire length of the simulated surface pollution source. Of course, if the landfill project contains detailed data on the scheme, the quantitative parameters and the rates of deposition activities, it is appropriate to take them into account by introducing appropriate stress periods and corresponding changes in the boundary conditions.

(vii) The results of the model calculations are presented as relative concentrations of SO₄ (in %), i.e. as a ratio between the current concentration CᵣSO₄ at a specific moment t and the initial (input) concentration CᵣSO₄. Normally, the value CᵣSO₄ = 100% is set as initial concentration over the entire spread of the new embankment and the background concentration in the subsurface section is set as CᵣSO₄ = 0%.

(viii) It is expedient to perform long-term prognostic calculations, i.e. the period of computer simulations shall be not less than 50 years.

Modelling tools

The mathematical 2D model of the conditions for the mass transport of pollutants in a variably saturated porous media is compiled with the software package VS2DTI Version 1.3 (Lappala et al., 1987; Healy, 1990; Hsieh et al., 2000). The algorithm of the programme uses a numerical finite difference method to solve the flow equation and the advection-dispersion equation (Bear, 1979; Healy, 1990).

The relations between pressure head, moisture content and relative hydraulic conductivity can be modelled using the functions proposed by van Genuchten (1980), Brooks and Corey (1964), Haverkamp et al. (1977), Rossi and Nimmo (1994), or by published values.

The initial hydraulic conditions are specified with a static equilibrium profile setting either the pressure head or the moisture content.

The boundary conditions include setting of the pressure head or the total head, as well as flow rate, recharge from infiltration, evaporation, transpiration, and boundary flow-through elements.

The processes describing mass transport include convective transport, molecular and mechanical dispersion, reversible elimination, irreversible elimination, and mixing. The processes that are the reason for a substance to enter/leave the liquid phase are simulated in two ways: (a) the dissolved mass is introduced into (or removed from) the model region by setting a certain concentration of the pollutant in the inflow or outflow boundary conditions; (b) the change in the concentration of the pollutant is simulated by the Henry linear isotherm, the Freundlich isotherm or the Langmuir isotherm, which describe the chemical reactions in the liquid phase or the reactions between the liquid and solid phases.

Conceptual model

The mathematical model for estimating the potential subsurface contamination caused by the designed new CCPs landfills in the area of the internal embankments of Troyanovo-North open-cast mine is developed in accordance with the following prerequisites:
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(i) Model area. Comprises the hydrogeological section in the range of the designed new embankments along Line 278 in the section from m+35200 to m+36000 (Figure 2).

(ii) Hydrogeological units (HGU). As illustrated in Figure 2, two low-rank hydrogeological units are established in the near-surface section – upper low-permeability anthropogenic layer (HGU1) and lower low-permeability layer (HGU2). The upper anthropogenic layer is an old embankment of mixed materials - clay from the overburden and CCPs. The landfill materials are uncompact and highly inhomogeneous, which presupposes their hydrodynamic heterogeneity and trend of differential settlement. The embankments thickness is usually between 25 and 30 m. The lower layer covers part of the intact clay-sand Neogene complex. It is represented mainly by Neogene clays and silty clays with calcareous inclusions. Layers and lenses of fine-grained and clayey sands are rarely observed in depth. The studied segment of the old embankment can be regarded as a part of the unsaturated zone. According to borehole data, the static groundwater levels are registered at an elevation of about 45-46 m in single lenses and seams in the intact Neogene complex.

Fig. 2. Conceptual framework of the two-dimensional models
1 – New embankment; 2 – Upper low-permeability anthropogenic layer (Model zone MZ 1); 3 – Lower low-permeability layer (Model zone MZ 2); 4 – Groundwater level; 5 – Rainfall infiltration; 6 – Leachate infiltration.

Table 1. Physical, hydrodynamic and mass transport field characteristics of the hydrogeological units

<table>
<thead>
<tr>
<th>Hydrological unit (HGU)</th>
<th>Model zone No</th>
<th>Volumetric mass density (\rho_n), mg/m(^3)</th>
<th>Porosity (n), %</th>
<th>Hydraulic conductivity (k), m/d</th>
<th>Longitudinal dispersivity (\alpha_l), m</th>
<th>Molecular diffusion coefficient (D_m), (m^2/d)</th>
<th>Distribution coefficient (K_{\text{SO}_4}), cm(^3)/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>HGU1</td>
<td>MZ1</td>
<td>2.0E+09</td>
<td>4.3E-01</td>
<td>2.5E-02</td>
<td>1.5E00</td>
<td>7.5E-04</td>
<td>3.1E-10</td>
</tr>
<tr>
<td>HGU2</td>
<td>MZ2</td>
<td>1.85E+09</td>
<td>5.0E-01</td>
<td>4.8E-03</td>
<td>8.0E-01</td>
<td>3.5E-04</td>
<td>4.9E-10</td>
</tr>
</tbody>
</table>

Remark: Main sources of the implemented averaged values of \(\rho_n\), \(n\), \(k\), \(D_m\), and \(K_{\text{SO}_4}\): (1) Stoyanov, 2007, 2019; (2) Spitz and Moreno, 1996; (3) Adams and Gelhar, 1992; (4) Enviro Base – software product of Waterloo Hydrogeologic Inc., Ontario Canada; (5) Unpublished data.

(iii) Hydrogeological parameters. The hydraulic conductivity \(k\) and the physical characteristics (density \(\rho\), porosity \(n\), etc.) of the two layers are defined according to data from in-situ observations and laboratory tests conducted for the study area (slug tests, tracer tests, granulometric analysis, petrophysical analysis, etc.). The distribution coefficient \(K_d\) (respectively, the sorption porosity \(n_s\) reflecting the fate of \(\text{SO}_4\) in the upper low-permeability anthropogenic layer is defined according to data acquired by conducted laboratory tests (tracer tests) with materials from Gypsum storage facility Nr 1 of TPP Maritsa East 2 (Stoyanov, 2007). The mass transport field characteristics (distribution coefficient \(K_d\), longitudinal dispersion \(\alpha_l\), molecular diffusion coefficient \(D_m\)) of the hydrogeological units, which are not laboratory established, are determined according to literature data for similar soil types (Adams and Gelhar, 1992; Spitz and Moreno, 1996; Enviro Base, 2003; Stoyanov, 2019). The values of the physical, hydrodynamic and mass transport characteristics, applied in the prognostic model, are presented in Table 1.

(iv) Rainfall recharge.

Infiltration rate \(W_i\). With an average annual value of precipitation of 550 mm and an average annual air temperature of 12.3 °C, the total discharge (surface and underground) is 186 mm/a. The infiltration rate, calculated according to Bredencamp (1990) for low-permeability soils, is 31 mm/a. It follows that the infiltration recharge is about 5.6% of the precipitation. Therefore, the infiltration rate \(W_i\) is equal to 8.5E-5 m/d.

Concentration of sulphate ions in rainfall. With some conditionality, it is accepted that the presence of sulphate ions in precipitation is negligible, i.e. \(C_{\text{SO}_4}\) = 0%.

(v) Source of contamination. This is the landfill leachate as illustrated in Figure 2. The model considers the fate and transport of the selected key pollutant \(\text{SO}_4\). The accepted values for the leachate infiltration rate \(W_l\) and for the concentration of sulphate ions \(C_{\text{SO}_4}\) over the entire area of the source are as follows:

Leachate infiltration rate \(W_l\). As precipitation is the only income element in the new embankments water balance, it is...
assumed that it is equal to the groundwater recharge from infiltration, i.e. \( W_r = 8.5E-5 \text{ m/d} \).

**Concentration of sulphate ions in leachate** \( C_{p,SO_4} \). According to the established way of presenting the model prognostications in relative concentrations, it is accepted that in leachate \( C_{p,SO_4} = 100\% \).

(vi) Period of computer simulations. Taking into account the very low water permeability of the two hydrogeological units, one can expect that the rate of mass transport processes will be low. Therefore, it is recommendable for the prognostic models of possible subsurface contamination to cover a period of 100 years.

**Composition of the prognostic model**

For structuring the prognostic model, the VS2DTI programme and the main prerequisites presented in the conceptual model are used.

The mathematical model is two-dimensional. It reproduces the fate and transport of highly mobile contaminants in the section along the profile illustrated in Figure 2. The determined low-rank hydrogeological units are simulated with two model zones M21 and M22. Each zone is set with its geometry and hydrodynamic and mass transport field characteristics corresponding to the real ones (Table 1).

An orthogonal grid with cell dimensions of 0.5 x 2.0 m is utilised for the spatial discretisation of the model area. The time of the computer simulation is divided into 100 stress periods, each lasting 1 year.

The relationship between pressure head, moisture content and relative hydraulic conductivity is modelled using the functions proposed by van Genuchten. In this case, for the variable residual moisture content (RMC) and for the isotherm parameters \( \alpha \) and \( \beta \) are used incorporated in the computer programme values for similar types of soil. The Henry linear isotherm is applied in order to model the solid-liquid reactions.

The initial hydraulic condition is specified as an equilibrium profile, which is set as the initial pressure head equals negative elevation head above a water table.

Along the lateral boundaries of the model in the saturated part of HGU2, according to the established groundwater levels, a boundary condition Specified total head is set, and in the unsaturated part of HGU1 and HGU2, a boundary condition Possible seepage face is accepted.

The upper boundary of the model area follows the elevation of the old embankment. It is divided into 3 parts – a central one, having a length of 560 m and two peripheral, having lengths of 150 m and 90 m, respectively. The central part outlines the bottom of the new embankment, where the leachate emissions come from, i.e. it marks the linear source of contamination.

A boundary condition Specified flux into domain is set along the upper boundary of the model area with the following input data: (a) in the central part of the profile, during the whole period of the model simulation, the pollutants enter with infiltration rate \( W_r = 8.5E-5 \text{ m/d} \) and input concentration of sulphate ions \( C_{p,SO_4} = 100\% \); (b) in the peripheral parts of the profile, during the whole period of the model simulation, pure rainwater enters with infiltration rate \( W_r = 8.5E-5 \text{ m/d} \) and concentration of sulphate ions \( C_{p,SO_4} = 0\% \).

**Results and discussion**

With the developed model, at the end of each stress period, a prognosis is made for the extent and degree of possible subsurface contamination. The results of the computer simulations of the fate and transport of the most mobile pollutants are illustrated with the obtained model solutions, presented in Figure 3, reflecting the distribution of sulphate ions after a period of 5, 50, and 100 years.

The model is also used in order to calculate the depth of the polluted zone \( D_{SO_4} \) (the contamination front) as a function of time \( D_{SO_4} = f(t) \) in the lowest part of the terrain – the sector at \( m+35685 \). The calculations are performed tracking the isoline of sulphate ions concentration \( C_{p,SO_4} = 0.5\% \). The obtained results are illustrated in Figure 4.

Based on the model solutions, a long-term prognosis can be made for the subsurface contamination beneath the new embankment. The mobile pollutants that have entered the old embankment move very slowly and the main direction of mass transfer is vertical. In 100 years, the pollution front advances to a depth of about 18-19 m, i.e. the vertical velocity of the pollutants is very low - about 5 mm/d.

The most intense contamination affects the upper part of the old embankment to a depth of 3-4 m, where the concentration of \( SO_4 \) is between 75 and 100\%. At depths above 10-11 m, the values of \( SO_4 \) concentration fall below 10\%. The contaminated zone expands laterally by about 5 m due to the processes of molecular diffusion and mechanical dispersion.

For the forecast period (100 years), the pollution will be limited in the old embankments and will not reach the intact clay-sand Neogene complex. Thus, there is no risk of groundwater contamination, taking into account also the low water permeability of the Neogene clays that compose HGU2. The main reason for the slow rate of the mass transfer processes and the limited spread of the contaminated area is the very low water permeability and the large thickness of the old embankment of mixed materials – clay from the overburden and CCPs.

**Conclusion**

The solutions obtained with the developed prognostic model show that for a period of 100 years the subsurface contamination caused by the designed new embankments in the area of Troyanovo-North open cast mine will cover only part of the old embankments without affecting the intact clay-sand Neogene complex. There is no risk of groundwater pollution. In hydrogeological aspect, the terrain is completely appropriate for deposition of coal combustion products from TPP AES Galabovo.

The presented prognostic model illustrates the great efficiency of the proposed methodological approach for preliminary assessments of the possible contamination of near-surface section and groundwater caused by landfills for deposition of CCPs, produced by coal-fired thermoelectric power-production facilities.

Our experience confirms that the same approach can be successfully applied in solving similar hydrogeological and environmental problems.
Fig. 3. Results of the computer simulations of the subsurface contamination caused by the new embankment

Fig. 4. Depth of the contamination front in the lowest part of the terrain – the sector at m+35685

Acknowledgement

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COMPARATIVE ANALYSIS OF THE TECHNIQUES FOR DETACHMENT OF NATURAL STONE BLOCKS FROM THE MASSIF WITH FLEXIBLE HIGH-EXPLOSIVE CHARGES AND BULK-EXPANDING CHEMICAL COMPOSITIONS

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ABSTRACT. Studies of foreign experience in the extraction of magmatic rocks for decorative and cladding purposes show a continuing trend for the use of high-speed explosives in the primary separation of the rock block from the massif. The belief that this is the cheapest way for primary extraction against the background of the prices for cutting of hard and highly abrasive rocks with diamond-rope, chain- and disk-stone cutters, makes quarry owners to put up with the losses from unwanted cracking of high-quality material. The authors undertook a series of experiments on samples of magma rock with hardness f = 16 according to Protodyakonov. The advantages and disadvantages of an alternative non-explosive technology for stone splitting with bulk-expanding mixtures were analysed. The results were compared with those using detonating cord charges to detach rock blocks with the same characteristics.

Key words: non-explosive stone splitting, bulk-expanding mixtures, smooth blasting, ornamental stone extraction

Introduction

The products extracted from dimension stone (DS) quarries are prismatic blocks of materials such as granite, gneiss, gabbro, diabase, marble, limestone, sandstone, slates and others. Most of them are preferred because of their aesthetic and attractive characteristics, namely colour, texture, polishability, etc.

Dimension stone blocks are mainly used in the building, making of sculptures and monumental tombs or ornamental facing materials for interior and exterior of buildings. The definition of rock facing materials covers rough blocks and finished products, but excludes crushed aggregates or stone dust consumed as raw material or recycled for the production of artificial stone.

Four major operations are used in quarries for rock-facing materials: removal of overburden and development of quarrying faces, primary extraction of lamellas, splitting of blocks to dimensions for transport and stone processing. Overburden removal, blocks cutting, splitting, handling, and transportation from quarry site to processing plant are known as the major quarrying operations (Abdollahisharif, Bakhtavar, 2009). Overburden and weathered rocks are usually loosened by blasting and can be removed using a dragline, a scraper, a front-end loader and a bull-dozer. After the surface is cleaned, a trench is made and a bench is formed across the width of the quarry. This provides an additional free surface that facilitates the extraction of subsequent blocks until the first horizon extending across the entire width and length of the quarry is seized or until sufficient space is provided to remove another key block opening a second horizon. The upper surface and the slope of the bench provide two free surfaces (upper and front of the prismatic block). Three additional cuts (surfaces) are made, which define the edges and the back. Those cutting surfaces are usually made with more precise cutting and splitting devices. Capital and operational costs and quarry life are influenced by the method employed for the extraction of dimension stones. Therefore, the selection process of an extraction method is a crucial problem in dimension stone quarries. Below those extraction methods are considered which can separate the desired blocks from the face intact rock (Bakhtavar et al., 2012). For this purpose, diamond wire cutters, chain stone cutters, blade diamond stone cutters, burners, water jet cutters, smooth blasting, and expansive mixtures are usually used.

The compressive strength of volcanic rocks in Bulgarian quarries of rock facing materials, where field experiments were performed, range from 130 MPa to 300 MPa. The dimensions of the extracted blocks are usually 1.2 - 2 m wide, 1.5 - 3 m long and thick to the nearest split plane. The blocks are separated manually using chisels and hammer to obtain the size and shape of the product sought. During the process of manual separation and sizing, about 50 - 75% of the stone is turned into waste. Because of this reason improved technologies for extraction are needed to reduce the formation of waste in DS mining. In small quarries for volcanic rocks, where a cutting machine cannot be used, controlled cracking in the desired direction by blasting, with minimal damage to the valuable material, is the main technique established after the 1980s (Dino, Cavallo, 2014).

Each unwanted crack in the dimension stone divide it into small pieces as waste or turns it into product with very low value (Muhammad, 2012). Therefore, finding an improved blasting technique in the extraction of stone blocks is of paramount importance. Given these aspects, tests for the formation and development of macro-cracks in the desired direction are carried out in dimension stone quarries, while preventing the unwanted appearance of micro-cracks in the extracted block and the residual rock. In the present research work the analysis was made on the basis of field tests.

Theoretical foundations

The explosive energy released in the rock, in addition to performing useful work of fragmentation and displacement, can cause damage to the residual array in the form of unwanted cracks at the micro-level (Mollova, 2019b). Significant efforts have been made in recent years to investigate and minimise blast damage in conventional blasting operations (Belin, Mollova, 2021). The work on estimating the extent of the damage to the stone is very scarce. These damages should be reduced in the extraction of natural stones, where a small amount of explosive energy is used for primary separation from rocks or for splitting of separated blocks. In some situations, such as contour blasting, digging tunnels and underground chambers, unwanted damage must also be kept to a minimum.
Controlled blasting is useful for the long-term stability of underground workings. Well-planned contour blasting indirectly reduces excavation costs in addition to stability (Zhang, Chang, 1999).

The overhangs in the ceiling and the walls of the underground chambers and tunnels require a large amount of fasteners and reinforcement. Cracking and damage to the residual rock can lead to safety problems due to the collapse of stones, as well as to additional costs incurred to maintain the layers (Mollova, Penev, 2020).

The degree of damage is not only a function of the explosive-seismic impact, but is also related to other site-specific parameters such as rock strength and geological structural characteristics (Zhang, Chang, 1999). The cracking of the rocks creates an imbalance in the energy distribution of the explosion (Singh, 2005). The presence of joints also affects the attenuation of stress waves (Mollova, 2019a). In addition, the presence of clay material in the cracks, its potential for swelling and thickness contribute to the poor quality of the rock mass, which in various situations can lead to excessive fragmentation or slight cracking. As a result of the presence of cracks in the stone blocks, the recovery from the sold product decreases.

All controlled blasting techniques such as cushion-blasting, pre-splitting and smooth blasting have one common goal, namely to better distribute the energy delivered to the rock mass during the detonation of the explosive, so as to control the effects of crushing and breaking (Penev, Mollova, 2020). They are used in blasting operations for extraction of ores and aggregates, when unwanted cracking in the main massif must be avoided. But these techniques develop micro-level cracks that are not desirable in the extraction of rock facing materials (Zhang, Chang, 1999). For this reason, flexible linear decoupled charges with a strongly reduced concentration of high explosive are used for the cleavage of dimension stone blocks. In the second half of the 20th century, the practice required the use of detonating cords (DC) as convenient for work flexible extended charges for detachment. Manufacturers offer DC with different power, determined by the content (weight) of pentaerythritol tetranitrate (PETN) per linear meter of cord. The correct sizing of the charge in relation to the diameter and length of the blast holes is crucial for the presence or absence of random radial cracks and for the controlled displacement of the separated rock mass (Koprev, 2016). Another factor in reducing parasitic cracks is the centre of the charge in the blast hole, which prevents it from touching its walls (Cardu et al., 2005). It is essential to avoid even very small irreversible deformations along the blast holes by the presence of a stemming or damping material around the DC threads in the holes (Koprev, 2012).

To protect the most expensive decorative-facing rock materials from the formation of micro-cracks, in the primary extraction from the massif (as well as in the secondary splitting of the block), instead of explosive impact, controlled cracking with volume-expanding chemical compositions is applied (Muhammad, A., 2012). In recent years, this technique is used in the extraction of marble, breccia, granite and other rocks with high hardness and good cleavage. The method is ineffective in soft rocks. The technology is based on the property of certain chemical compounds to "absorb" water when wet by binding it to their own molecules in the so-called chelating complexes. Upon drying of the material, the water molecules appear to be part of the crystal lattice of the compound. This leads to a drastic increase in the coefficient of volumetric expansion (Stoycheva, 2019). Thus, these substances, when placed in drilled holes and in contact with water, are able to harden and expand after some time, creating stresses in the rocks up to 40-45 MPa. The essence of the technology is the same as in the drilling-wedge and drilling-blasting method. Vertical and horizontal holes are perforated along the contours of the block with the drilling mechanisation (jack-hammers, jumbos or drills). The effective range is from $\phi$ 32 to $\phi$ 55 mm. At smaller diameters, the percentage of volumetric expansion is insufficient to develop destructive stresses. With larger diameters, the cost of materials becomes inexpedient against the background of the useful effect. According to the literature, the distance between the holes depends on their diameter, the specific conditions, the type of rocks extracted, and the expandability of the chemical compound. Some manufacturers claim that as the depth of the holes increases, the distance between them can increase. The stronger the rock, the smaller the distance between the perforations. Most often the distances between the holes are from 100 to 400 mm, and the free surface 400 to 600 mm. The depth of the holes is from 2/3 to 3/4 and in very rare cases equal to the full size of the block. The height of the bench with this technology is relatively small - up to 2.5 m. When the benches are higher, the separation of the blocks takes place in stages from the half-steps. The time for destruction of the rocks (splitting takes place along the line of drilling holes) varies from 10 to 24 hours, and factors influencing this time are: the type of chemicals used, the properties of the rocks and the temperature of the environment and the rocks. The time for splitting the rocks can be reduced by shortening the distance between the holes, but this in turn increases the time and cost of drilling operation. It is possible to separate very large blocks from the array with a volume of up to 2000 m³. Rock-breaking stresses could form macro-cracks not exceeding the diameter of the holes. Powdered substances are available, packed in plastic bags to protect from humidity. The powdered material is mixed with 20 to 40% water and the resulting slurry is poured into the holes. Chemical reactions begin immediately. The expanding mixture exerts the same pressure in each hole and the block separates in the direction of the drilled holes. This technology for extraction of rock blocks is most often applied in combined ways of making vertical longitudinal sections (cuts), as the volume of drilling works is reduced by 30 to 40% compared to the drilling-wedge method. Products from different manufacturers are available on the market. The principle of action and the main ingredients are identical, the differences being in the additives for speeding up and stabilising the process. A specific feature is the temperature range for efficient operation of these compositions. Below 0 °C the water freezes and the technology becomes inapplicable. As the temperature rises, the chemical processes accelerate and the efficiency increases. At temperatures above 30 °C the reaction becomes violent and the risk of accidents increases.

**Experimental part**

The tests for assessment of damages caused by compressive stresses were performed in quarries for extraction of volcanic rocks for decorative - monumental purposes with a Protodyakonov hardness coefficient $f = 16$. To compare the effects of the impacts, it was necessary to conduct tests under approximately the same conditions.

For the comparative analysis the authors made two groups of experiments:
Results and discussion

The use of flexible linear charges allows for an even distribution of the shock wave and the pressure of the explosive gases along the entire length of the blast hole. Thus, the compressive stresses on the walls of the hole are the same and the chance of forming a crack in an undesirable direction becomes smaller.

In the experimental blasting with a single thread DC 12 g/m (Experiment - 1) a slight crack of the rock body in the intended direction was observed, accompanied by a slight displacement of DC, inserting the knots to the bottom with the help of a wooden rod. Thus, the amount of charge in one hole was about 68 g PETN (excluding the content of 12 cm DC protruding outside the hole). The first hole was left with an "air gaps", the second was filled with sand around the charge, and the third was filled with water gel. The ends of the three DC-threads were joined with a short section of DC in a common chain.

Experiment - 4: Splitting of a rock piece with a centralised fixed charge of DC 24 g/m. In each of the three explosive holes we placed two strands of DC, wrapped in a "casing" of corrugated cardboard. Thus, the amount of charge in one hole was about 43 g PETN (excluding the content of 20 cm DC protruding outside the hole). The ends of the three DC-threads were joined with a short section of DC in a common chain.

The initiation of the explosive chains was performed with electric detonators with instantaneous action. To reduce the effect of the air-blast, the exposed parts of the DC network were covered with a thick layer of sifted sand.

Splitting of rock blocks by expanding mixtures

Three attempts were made for the second group of experiments. Untightened (free) boulders of the same type and size were used for each experiment. The selected splitting strips were about 1.5 m long with a stone thickness of about 1.0 m. Thus, we achieved almost the same dimensions of the cutting areas of 1.5 m². The technology uses the same pre-drilled holes in the rock as the blast method. In each of the three stones, parallel vertical holes with a length of 0.80 m and a diameter of φ = 38 ± 42 mm were drilled in a line.

For Test - 1, five holes were perforated every 0.20 m with a distance of the peripheral holes to the sides of 0.35 m.

For Test - 2, four holes were perforated every 0.30 m with a distance of the peripheral holes to the sides of 0.30 m.

For Test - 3, three holes were perforated at 0.40 m with a distance of the peripheral holes to the sides of 0.35 m.

The composition was unpacked and homogenised with cold water on the site, immediately before use. The ratio used was from 280 to 320 ml of water per 1 kg of dry mix, depending on the weather conditions. The finished solution was poured expeditiously directly into the cleaned from dust dry holes. The test boulders were exposed to the chemical expander for the 24 hours prescribed by the supplier and were periodically monitored for changes.

The average market price per 1 kg of the chemical expanding composition used is around EUR 1.75. The average consumption when filling a 1 m hole with a diameter φ 40 mm is about 1.5 kg of dry matter in the form of an aqueous solution. It can be assumed, that the value of the chemical expander consumed per linear meter of perforation (φ 40 mm) is about EUR 2.63.
of the treated block. Due to the low charge and the buffering role of air, sand and water gel, which further reduces the explosive effect on the rock - after the excavation, on the block and the array no parasitic cracks were observed on the chipped surfaces. The value of spent explosives, excluding the cost of drilling and damping water gel was 5 EUR for 3 m$^2$ of cut surface (for 7 m DC $\times$ 0.5 EUR/m = 3.50 EUR and for 1 electric detonator $\times$ 1.5 EUR = 1.5 EUR).

In the experimental blasting with double thread DC 24 g/m (Experiment - 2) a good splitting of the rock body in the intended direction was observed, accompanied by a satisfactory displacement of the treated block. Due to the buffering role of air and sand, no visible cracks were observed on the chipped surface on the block and the array. A slight single crack was observed along the channels remaining from the third hole (with the water gel). A probable reason is the formation of a hydro-shock wave due to the high density of the water gel. The value of spent explosives, excluding the costs of drilling and damping water gel was 8 EUR for 3 m$^2$ of cut surface (for 13 m DC $\times$ 0.5 EUR/m = 6.50 EUR and for 1 electric detonator $\times$ 1.5 EUR = 1.5 EUR).

In the experimental blasting with a triple thread DC 36 g/m (Experiment - 3) there was a serious detachment of the rock body in the intended direction, accompanied by a large displacement of the treated block. Despite the buffering role of air and sand, visible cracks were observed on the chipped surfaces. Longitudinal and radial cracks were seen in the channels remaining from the three holes. The damages were lesser at the first hole (with the air stemming). The value of spent explosives, excluding the costs of drilling and damping water gel was 11 EUR for 3 m$^2$ of cutting surface (for 19 m DC $\times$ 0.5 EUR/m = 9.50 EUR and for 1 electric detonator $\times$ 1.5 EUR = 1.5 EUR).

In the experimental blasting with a centrally fixed charge of DC 24 g/m (Experiment - 4) a very good crack through the rock body in the intended direction was observed, accompanied by sufficient displacement of the treated block. Due to the buffer role of the corrugated cardboard, no visible cracks were observed on the block and the array on the chipped surfaces. The value of the spent explosive materials, excluding the costs for drilling works and centralizers made of corrugated cardboard, was 8 EUR for 3 m$^2$ of cutting area (for 13 m DC $\times$ 0.5 EUR/m = 6.50 EUR and for 1 electric detonator $\times$ 1.5 EUR = 1.5 EUR). Given the satisfactory results achieved by splitting and displacement without visible damage, the authors take this experiment as a milestone in calculating the average value to obtain 1 m$^2$ of cutting surface using bulk-expanding chemical reagent.

During the separation with the volume-expanding composition of Test - 1, a crack was noticed along the line between the flooded holes as early as the sixth hour after filling them with the solution. By the 12th hour the crack had reached a width of 10 to 12 mm. By the 24th hour, a slit crack with a width of 28-30 mm and no distortion had formed. The value of the consumed materials, excluding the costs for drilling works, was EUR 10.50 per 1.5 m$^2$ of cut plane. For the filling of 5 holes of 0.8 m each (4.0 m totally), using 1.5 kg/m reagent, 6.0 kg of dry mixture was utilized. The reagent costs 1.75 EUR/kg, so the total was 10.5 EUR.

During the splitting with a volume-expanding composition of Test - 2, a crack was observed along the line between the flooded holes about 10 hours after filling them with the solution. By the 16th hour, the crack had reached a width of 13 to 15 mm. By the 24th hour, a 24-26 mm wide fissure had formed and distorted due to the presence of a vein. The value of the consumed materials excluding the costs of drilling works was EUR 8.40 per 1.5 m$^2$ of cutting plane. For the filling of 4 holes of 0.8 m each (3.2 m totally), using 1.5 kg/m reagent, 4.8 kg of dry mixture was utilized. The reagent costs 1.75 EUR/kg, so the total was 8.40 EUR.

When splitting with a volume-expanding composition of Test 3, the first crack along the line between the filled holes appeared after the 12th hour of their filling with the solution. By the 20th hour, the crack had reached a width of 10 to 11 mm. By the 24th hour, a gap 18-19 mm wide had formed and distorted due to the presence of a joint. The value of the consumed materials excluding the costs of drilling works was EUR 6.30 per 1.5 m$^2$ of cutting area. For the filling of 3 holes of 0.8 m each (2.4 m totally), using 1.5 kg/m reagent, 3.6 kg of dry mixture was utilized. The reagent costs 1.75 EUR/kg, so the total was 6.30 EUR.

Given the equal distance between the perforations compared to the experiments with detonating cord and the achieved satisfactory results of cleavage and displacement without significant damage to the material, the authors take this experiment as orientation in calculating the average value to obtain 1 m$^2$ of cutting surface using bulk-expanding chemical reagent.

**Conclusions**

Based on the proceeded experiments, a comparative analysis of the costs of splitting stone blocks of volcanic origin during their extraction in DS quarries was made, by means of instantaneous explosive action with DC and slow impact with bulk-expanding chemical mixtures. The average value for the formation of a 1.0 m$^2$ cutting surface by smooth blasting with a flexible linear charge of DC without the application of visible parasitic cracks on the surfaces of the material amounts to about 2.70 EUR/m$^2$.

The minimum value for effective formation of 1.0 m$^2$ of cut plane by volume-expanding chemical mixture, without causing significant damage to the surfaces of the material was about 4.20 EUR/m$^2$.

Splitting of rock blocks with detonating cord is the fastest and cheapest method for extraction and secondary processing of dimension stones, but the risk of damage with micro-cracks continues to affect the performance of the final products. Due to the high performance of PETN charges, the relative cost of drilling can be reduced by increasing the distance between the bore-holes. This will contribute to even higher economic efficiency of blasting activities. The results of the experimental blastings show that additional research and field tests are needed to improve the control over the distribution of explosive energy to concentrate the compressive stresses in the desired direction, namely between the perforations along the breakaway loop. In practice, this will lead to an increase in the efficiency of the charges from the DC.

The main advantage of expanding mixtures (despite their higher cost) over explosive energy methods is the simplified unlicensed acquisition, transportation, storage and use. Another advantage of the technology for rock splitting with bulk-expanding compositions is the negligible danger of formation of micro-cracks in the decorative stones. Additional advantage of this methodology is the lack of need for expensive equipment.
and certified qualified personnel for its implementation. The main disadvantages are the slow action and the narrow temperature interval for work. When optimising the processes, the methodology has the potential to replace blasting activities in the extraction of expensive magmatic rocks near protected sites.

The authors are planning to continue their research in the following areas:
- testing of charges from DC with axial fixation in the blast hole in the housing for directing the explosive energy, with stemming to seal the space between charge and walls of the hole;
- testing of DC charges with axial fixation in blast holes with local slots (notches) for directing the split in the desired direction. Pre-cutting the walls of the blast hole would increase the stress concentration in the area, and it is expected that the crack should start from the notched area.
- application of technology with expanding chemical compositions in the primary separation of rock blocks from the main massif.

References


BIOTECHNOLOGICAL RECYCLING AND RECOVERY OF METALS FROM SECONDARY RAW MATERIALS THROUGH BIOGENIC SYNTHESIS OF NANOPARTICLES

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ABSTRACT. The waste electrical and electronic equipment (WEEE) is an important secondary source for renewable extraction of valuable metals and raw materials. The mineral biotechnologies are promising alternative to the current industrial chemical technologies for waste treatment, which are often accompanied with negative environmental impact. Here we report a systematic biotechnological strategy for recycling, recovering and extraction of metals from WEEE as biogenic formed nanoparticles. The process is based on two general steps – bioleaching (through autotrophic/heterotrophic bacteria), and extraction from the effluent as biosynthesised nanoscale materials. The obtained analytical data revealed that copper was bioleached in the form of nanoparticles, the efficiency being more than 90 %, which was the highest achieved value in comparison with the other metals. The recovered content of gold was less than 50 %, but the efforts for improvement of microbial leaching efficiency of Au are still in progress. The reported eco-friendly biotechnological approach enables proper implementation of new resource recovery-oriented recycling strategies with reduced risk of negative impact on nature.

Key words: biotechnological recycling, secondary raw materials, nanoparticles

Introduction

The waste of electrical and electronic equipment (WEEE), which is often referred to as electronic waste (E-waste), is discarded devices that are at the end of their exploitation life and cannot be utilised by consumers anymore (Baldé et al., 2015). WEEE is being hazardous to the environment, in particular the printed circuit boards (Ghosh et al., 2015). On the other hand, E-waste could be considered as an important secondary source of valuable and critical metals. The elemental composition of the discarded devices might be often highly variable and complex (Cui and Forsberg, 2007). However, numerous references have reported significantly higher contents of copper, iron, aluminium, and nickel, as well as lower amounts of gold, silver, and palladium (Yamane et al., 2011) than in natural ores.

The metal recovery from WEEE as a secondary source is necessary for the sustainable development of economy, for supporting the conservation of the primary sources and preventing further environmental contamination (Robinson, 2009). There is a huge number of conventional methods (particularly in the chemical and metallurgical processing sectors) for recovery of metals from secondary raw materials (Ilyas and Lee, 2014), but in recent years the research efforts have been focused on the development of environmentally friendly biotechnological treatment and recycling strategies (Nancharaiha et al., 2015; Işildar et al., 2019). They may offer promising alternatives to the pyrometallurgical technology, because of the designed selectivity towards critical and valuable metals, lower environmental impact and cost-effectiveness (Morin et al., 2006). The bioprocessing includes various microbial techniques as bioleaching, bioreduction, biosorption, etc., in which a wide and diverse range of chemolithotrophic, heterotrophic and thermophilic microorganisms are involved (Xiang et al., 2010; Natarajan and Ting, 2014). Most of them have a high tolerance to the heavy metal toxicity (Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans and Leptospirillum ferrooxidans). These microorganisms have been tested to mobilise base and precious metals (Cu, Fe, Ni, Zn, Au, Ag, Pt, Pd, etc.) from discarded printed circuit boards (PCB) through biochemical mobilisation mechanisms.

In this report a biotechnological strategy was developed for recycling, recovering and extraction of both critical and conventional metals as nanoparticles from WEEE. The emphasis was put on copper and gold, as well as on other metal contents from PCB.

First, the metals were bioleached in a two-steps autotrophic/heterotrophic biorecovery strategy through redoxolysis, acidolysis and complexolysis mechanisms. For that purpose the bioleaching media that contained E-waste was inoculated with cultures of chemolithothrophic acidophilic iron- and sulphur-oxidising microorganisms (Išildar et al., 2016). In this case, the biogenic sulphuric acid and ferric iron act as lixiviants via respectively, acidolysis and redoxolysis bioleaching mechanisms (Bas et al., 2013). The metals were mobilised to their ionic state in the media via either acidolysis or redoxolysis. The copper was predominantly found in PCB and it was bioleached by a mixture of autotrophic iron- and sulphur oxidiser Acidithiobacillus ferrivorans and Acidithiobacillus thiooxidans. The gold was removed from WEEE by Pseudomonas putida at ambient temperature (Brandl, 2008).

Second, biosynthesis of nanoparticles and extraction of these metals from the concentrates was accomplished. Bacteria and fungi microorganisms are suitable for metallic nanoparticle production through secretion of NADH dependent enzymes necessary for the extracellular processes.

The mechanism for nanoparticles formation was following the designed strategy: A) Metal ions are trapped on the surface or within microbial cells (De Yoreo and Vekilov, 2003). Gold, silver and palladium ions are attracted due to the electrostatic interactions with the enzyme carboxylate groups of the negatively charged cell wall (Sneha et al., 2010). (B) The
cations are reduced by reducing agents (reductase enzymes and proteins, exopolysaccharide, and electron shuttle quinones) or precipitated as nanoparticles with different size and shapes (Singh et al., 2016). As a result, the inorganic metal residues were deposited on the surface of precipitations through adsorption or co-precipitation (Hohmann et al., 2010).

Experimental Procedures

Grinding and preparation of E-waste for bioleaching treatment

TV circuit boards and PCB were used as manufacturing scrap in our experiments. The samples were initially crushed in a rotary cutting shredder to a size of 2-3 mm and then grinded to 200-250 μm by ultracentrifugal mill (Retsch, Model ZM200 Ultra). The grinded samples were used for the further bioleaching experiments in microbiological suspension. Their metal composition was determined by chemical analysis (the concentration of iron was determined using titration with KMnO₄ and atomic absorption spectrophotometry (Perkin Elmer AAAnalyst 400). The samples contained mainly copper (19-22 %), iron (1-5 %), aluminium (1-3 %), nickel (< 1 %) and precious metals as gold, palladium and platinum in trace concentrations (< 0.001 %). Additional amount of pyrite (up to 40 g/L) was mixed with the sample as a source of iron and sulphur in order to initiate the bioleaching processes.

Metals recycling and biorecovery by cultivated microorganisms

A mixed culture of mesophilic bacteria (A. ferrooxidans, L. ferrooxidans, A. thiooxidans) was used for the biorecovery stage of the metals.

The microbiological suspension was grown and maintained on pyritic materials. The composition of growth media was 1.5 g/L (NH₄)₂SO₄, 0.5 g/L MgSO₄.7H₂O, 0.5 g/L KH₂PO₄ and 0.1 g/L KCl. For the bioleaching reaction 200 mM Fe(II) was added to the culture and subcultured at pH 1.7, 30 °C. The acidithiobacillus strains were grown also in a nutrition medium containing: 2.0 g/L (NH₄)₂SO₄, 0.25 g/L MgSO₄.7H₂O, 0.1 g/L KH₂PO₄, 0.1 g/L KCl, 8.0 g/L FeSO₄.7H₂O and 10 g/L elemental sulphur. pH was adjusted to 2.5 by H₂SO₄ and the cultures were inoculated with 5 % growth medium and incubated at 30 °C. The residue of the first bioleaching step was collected, filtered, left to dry overnight, and sterilised before the second step.

The sterilised residue was then subjected to secondary bioleaching by adding the dried material of the first bioleaching step to cultures of cyanogenic bacteria as Pseudomonas putida. The cyanogenic strains were grown in nutrient broth containing: 1.0 g/L meat extract, 2.0 g/L yeast extract, 2.0 g/L peptone, and 5.0 g/L NaCl for subculturing and in glycine-supplemented medium for cyanogenic activity and bioleaching reactions. The pH of suspension was adjusted to 7.3 with 1 M NaOH. The microbial cultures were subcultured with 1% (v/v) in 100 mL growth medium in 300 mL Erlenmeyer flask and incubated at 30 °C at a rotation speed of 150 rpm (Brunswick Innova 2000, USA).

The growth of bacteria was monitored by measuring optical density (OD) at 600 nm.

The bioleaching experiments were conducted in 250-mL Erlenmeyer shake flasks. Freshly grown and active bacterial culture (10⁷-10⁸ cells/mL) was applied as inoculum (10 mL). Erlenmeyer flasks were placed on an orbital shaker operated at 35 °C. During the biorecovery process aliquots of 1 ml were taken and used for elemental analysis of the dissolved metals by atomic absorption spectrophotometry. pH and redox potential were also used to monitor the microbial activity.

Bio synthesis of nanoparticles from the bioleached dissolved metals

A. Primary treatment of the pregnant leach solutions (PLS) with fungus Fusarium oxysporum.

To accomplish the biosynthesis of nanoparticles (mainly CuS, CdS, ZnS and Au) the fungus Fusarium oxysporum was used, which was kindly provided by Saitama University, Japan. The fungus was cultivated at 30 °C in Petri dishes with growth nutrition medium containing 20 % potato, 2 % dextrose and 2 % agar. Four-day old fungal spores were inoculated into 500 ml flask containing 100 ml medium (0.3 % malt extract, 1.0 % glucose, 0.5 % peptone and 0.3 % yeast extract) in order to initiate the fermentation. The flask was placed in a shaker-incubator (Brunswick Innova 2000, USA) for 96 hours at 30 °C and 160 rpm.

After completing the fermentation period, the mycelia were collected through centrifugation. They were washed with MilliQ water under sterile conditions. Further these mycelia were suspended in 100 ml of solution containing recovered Cu²⁺ with concentration around 0.001 M at pH = 5.0 – 5.5. The Erlenmeyer flasks were transferred into the shaker-incubator and kept there for 96 hours at 30 °C and 160 rpm. After that the biosynthesised nanoparticles were extracted (as mentioned above CuS, CdS, ZnS and Au) by centrifugation (14700 rpm for 30 min).

B. Secondary treatment of the residue PLS with Bacillus cereus.

The residue media of PLS was additionally treated with Bacillus cereus to extract the rest of precious metals (mainly Au and trace amount of Pt or Pd).

The bacterial culture was incubated in the shaker for 24 hours at 30 °C and 160 rpm. After obtaining the microbial biomass, the medium was centrifuged and bacteria were inoculated with the residue effluents containing dissolved gold. The microsuspension was incubated at 37 °C and 200 rpm for 24 hours. The gold nanoparticles were extracted by centrifugation (14700 rpm for 30 min).

Nanoparticle characterisation

The presence of nanoparticles was confirmed by absorbance spectra (UV-VIS Jasco analytical spectrophotometer, model No V-570) and 200 kV scanning transmission electron microscope (STEM, JEOL 2010F), equipped with a field emission gun and EDX spectrometer. The solution containing Au nanoparticles has a maximum absorbance peak at 500-550 nm due to the surface plasmon resonance (SPR).

EDX elemental analysis was used to prove the presence of Cu, Cd, Zn and Au. For this aim the nanoparticles samples were freeze-dried and the obtained powder was heated up to 300 °C for 1 hour. EDX spectra were recorded under 30° specimen tilt in high angle annular dark field (HAADF) STEM mode with 1 nm scanning electron probe size to ensure improved EDX signal-to-noise ratio.
Results and Discussion

Chemical analysis of the discarded PCB

The chemical analysis of the PCB waste showed a variety of metals as presented in Table 1. The copper (Cu) concentration was the highest one (around 20 %) in all various PCB types. Cu, iron (Fe) and aluminium (Al) were the other common elements among the assayed metals with concentrations around 3% and 4%, respectively. The mobile phones showed higher concentration of copper and gold than the other E-waste, which is due to their design and compact size. A notable variation in the concentrations of Al, Ni, Zn and Cd was determined too.

Table 1. Metal concentrations (mg/g) in the discarded PCBs

<table>
<thead>
<tr>
<th>Element</th>
<th>Computer parts</th>
<th>Desktops</th>
<th>Mobile phones</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>102.3 ± 5.1</td>
<td>201.8 ± 9.7</td>
<td>229.8 ± 8.5</td>
</tr>
<tr>
<td>Al</td>
<td>16.3 ± 3.9</td>
<td>34.8 ± 2.1</td>
<td>9.8 ± 3.7</td>
</tr>
<tr>
<td>Fe</td>
<td>3.3 ± 0.1</td>
<td>48.8 ± 7.3</td>
<td>39.7 ± 2.4</td>
</tr>
<tr>
<td>Zn</td>
<td>0.27 ± 0.01</td>
<td>4.9 ± 1.1</td>
<td>3.7 ± 0.1</td>
</tr>
<tr>
<td>Ni</td>
<td>0.88 ± 0.02</td>
<td>2.5 ± 0.2</td>
<td>10.4 ± 0.8</td>
</tr>
<tr>
<td>Cd</td>
<td>0.11 ± 0.01</td>
<td>0.18 ± 0.01</td>
<td>1.1 ± 0.1</td>
</tr>
<tr>
<td>Au</td>
<td>0.034 ± 0.002</td>
<td>0.023 ± 0.001</td>
<td>0.335 ± 0.002</td>
</tr>
</tbody>
</table>

Two steps bioleaching of metals

First step – bioleaching by acidophiles microorganisms. The copper was bioleached from PCB waste with very high efficiency, which was over 90 % (as shown on Figure 1). The control experiments proved that the acidophilic microorganisms A. thiooxidans and A. ferrivorans were responsible for the mobilisation of Cu from the waste in the aqueous suspension. During the process pH of the effluent might slightly decrease.

Second step – bioleaching by cyanide producing heterotroph microorganisms. After leaching of Cu, the chemical analysis proved that significant amount of Au still remained in the residue, containing waste materials. To extract the gold components, the remaining material was treated with cyanide producing P. putida strains. The gold leaching by biogenic cyanide is presented on Figure 2.

By this approach, the achieved highest gold recovery in our experiment was around 30 %, but some amount of Au (15-20 %) has been mobilised during the bioleaching with acidophiles. The experiments for improvement of microbial leaching efficiency of gold are still in progress. The experiments also demonstrated a correlation between the biogenic cyanide concentration and efficiency of gold mobilisation. Stoichiometrically, it is shown on the chemical reaction below:

\[
4\text{Au}^0 + 8\text{CN}^- + \frac{1}{2} \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Au(CN)}_2^- + 4\text{OH}^-
\]
The consumption of cyanide might be an indication that there is another precious metal or cooper, which has been not leached in the previous step. In addition, Zn, Ni and Fe form stable complexes with CN⁻. At high concentration, these metals might consume the cyanide contents and the bioleaching process of gold will be blocked. The process of cyanidation is dependent on pH and the leaching of gold is typically carried out in alkaline conditions (pH > 10.5). Therefore, the higher pH favours the metal mobilisation efficiency. Nevertheless, in the performed biotechnological experiments an optimum pH should be used in respect to the bacterial physiological requirements.

Nanoparticles synthesis by microorganisms

The obtained pregnant leach solutions with dissolved metals were finally subject to treatment with microorganisms for biogenic synthesis of nanoparticles. pH of solutions was adjusted to pH = 5.5, and the PLS were inoculated with *Fusarium oxysporum* and *Bacillus cereus* to obtain nanoparticles containing Cu, Zn, Cd, Au, etc. As mentioned above, the microorganisms have several mechanisms for biomineralisation or formation of minerals with nano-size on their membrane. Some of the mechanisms are not yet completely understood, especially the forming of gold nanoparticles on the fungal mycelia. Probably the metal reduction occurred thanks to NADH and NADH-dependent nitrate reductase enzymes, which act as a carrier and are responsible for the electron transfer to the cation (Ahmad et al., 2002). The formation of mineral depositions containing nanoparticles on the cell walls of microorganisms was observed by transmission electron microscope, as shown on Figure 3. In the control experiment (Figure 3A) the smooth structure of the cell wall can be seen and there are no biomineral depositions, they appear on the next image (Figure 3B), which is the case of nanoparticle synthesis.

![Fig. 3. Transmission electron microscopic images of (A) microorganisms used for nanoparticle synthesis as control experiment. (B) Microorganisms producing biomineralisation on their membrane envelops. Scale bars for A and B = 1 μm.](image)

Microscopic characterisation of the biogenic produced nanoparticles

The biosynthesis of nanoparticles was performed through a two-steps process. During the biosynthesis, the colour of the medium gradually turned to black, which was an indication of the successful biogenic synthesis of nanoparticles (or nanoscale materials). The experimental observation of colour change was significant in the primary treatment of PLS with the fungus *Fusarium oxysporum* and was due to the formed metal sulphide nanoparticles. A precipitated sample (pellet) was obtained from the microbial suspension with aim to analyse the nanoparticles size, shape and elemental composition. As shown on the dark-field STEM micrographic image on Figure 4A the nanoparticles were varying in size, but most of them have a diameter less than 10 nm. They have different shapes such as circular, triangle, or complex. In addition, most of them tend to form aggregations (it is hard to find single dispersed nanoparticles on the image). From the STEM image it is notable that the nanoparticles differ in contrast. The reason is that they contain different metal composition. EDX analysis of the aggregation on the micrograph (Figure 4B) revealed the presence of metals as Cu, Zn, Cd (probably some amount of Ag) and Au (Loukanov et al., 2010). The X-ray peaks of platinum are close to those of gold, so probably the sample might contain some trace amount of Pt or other precious metals.

As shown in the micrographic image the nanoparticles tend to form aggregations. It is difficult to distinguish what is the chemical composition in each individual particle. The EDX spectrum includes the signal emitted from all captured objects. Based on the contrast difference we can distinguish formation of nanoparticles with different elemental composition. The lower contrast particles are built from lighter elements and the higher contrasted from a heavier one.
In addition, the chemical and physicochemical processes as reduction, precipitation, co-precipitation, and adsorption are responsible for the formation of the aggregations observed in STEM. In the current report the nanomaterials were not separated based on their chemical composition. Such separation is possible by chromatography based on their different size and weight, and this research is in progress. However, the developed environmentally friendly method enables reliable recovery and extraction of toxic metals from E-waste thanks to their transformation into nanomaterials, which are easy to precipitate and separate from the concentrate.

Conclusion

In this study, we developed versatile biotechnological state-of-art method for recycling, recovery and extraction of metals as biosynthesised nanoparticles from E-waste. It has numerous advantages as (1) potentially better environmental and eco-friendly profile, (2) easy and practical operation, (3) better cost-effectiveness, and (4) potential for future development. Such bio-based eco-technology could be developed also towards more selectivity for metals’ recovery. It enables proper implementation of new resource recovery-oriented recycling strategies and may contribute to the reducing of the environmental risks associated with recycling processes of the waste electrical and electronic equipment.

Acknowledgment

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References


Bas A. D., Deveci H., Yazici E.Y., 2013. Biomechanical characterization of the biosynthesised nanoparticles. A Dark-field STEM image of nanoparticles aggregations. The nanoparticles have different contrast due to the different elemental composition. Scale bar = 10 nm (B) EDX-analysis of the aggregations. The presence of elements as Cu, Zn, Cd (probably Ag) and Au was detected in the observed sample.

Fig. 4. Scanning electron microscopic characterisation of the biosynthesised nanoparticles. (A) Dark-field STEM image of nanoparticles aggregations. The nanoparticles have different contrast due to the different elemental composition. Scale bar = 10 nm (B) EDX-analysis of the aggregations. The presence of elements as Cu, Zn, Cd (probably Ag) and Au was detected in the observed sample.


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OPTIMISATION OF LOCATION AND PERFORMANCE PARAMETERS FOR THE CRUSHING AND TRANSFER STATIONS IN THE DEEP OPEN PIT MINES

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ABSTRACT. When designing the strip mining methods at the deep open pits at the stage of preliminary studies, it is necessary to determine the optimum number and succession of relocation of crushing and transfer stations while developing the open pit. This cuts the transport costs and reduces the number of dump trucks required. An analytical dependence has been established to determine the optimum number of transfer points with their uniform location along the length and height of the open pit working area. The features of changes in the basic technological parameters of truck operation, depending on the number of crushing and transfer stations, the open pit size and output are studied. The conditions for simultaneous use of several crushing and transfer stations, their optimum number and performance have been determined; the economic benefits of using the flowcharts with multiple transfer points have been estimated. Optimisation of the number of transfer points reduces the required capacity of each crushing and transfer plant of up to 10-20 million tons/year. Reducing the required capacity of transfer points makes it possible to equip them with primary jaw crushers.

Key words: truck and conveyor transport, haulage level, crushing and transfer station

Formulation of the problem

One of the key focuses of engineering and technology development of open pit mining operations is the improvement of in-pit crushing and conveying systems (IPCC).

In recent decades, the global mining industry has implemented projects for which new designs of crushing and transfer points have been developed and high angle conveyors have been introduced. The overseas experience of open pit mining confirms the validity of key approaches to optimising the methods of deep open pit development, which are substantiated in the mining theory (Novozhilov, 1972; Yakovlev, 1989; Drizhenko, 2009).

One of the theoretical concepts of deep open pit mining is the principle of preference, all other conditions being equal, in which the proportion of electric energy in rock transportation is maximum.

The global economic trends encourage the engineers to seek the combined traffic patterns that minimise the diesel truck operation in the open pit mines. Provision of a rationale for principles of optimising the haulage level location when using the in-pit crushing and conveying methodology in the deep open pit mine is an important scientific and practical problem.

A particular feature of deep iron ore open pits in Ukraine is the use of combined traffic patterns based on truck-rail and truck-conveyor transport.

The location and design of transfer points have a significant impact on the truck operation and performance indicators of the open pit in general. As the open pit deepens, the haulage distance and the transport costs increase. In order to reduce the truck haulage distance and maintain it economically feasible, it is necessary to timely relocate the transfer points to deeper levels.

The traffic patterns of the Ukrainian iron ore open pits are characterised by a large proportion of IPCC process flows with the use of underground openings and immobile crushing and transfer points equipped with the KKD gyratory crushers. The use of mobile truck-to-conveyor transfer points and conveyor systems being capable of fast adaptation to the mining area development can increase the efficiency of mining operations in the deep open pit mines.

Analysis of researches and publications

The works of many researchers (Surface Mining, 1990; Drizhenko, 2009) analyse and generalise the technical solutions adopted in projects of foreign deep open pits with complex mining and geological environment. There is a long and intentional elaboration of mine opening systems throughout the entire period of field development.

There are many examples of effective cost reduction for open pit transport through the use of a system of underground conveyor ways (Figure 1), located outside the promising pit shell (Surface Mining, 1990).

![Fig. 1. Scheme of underground openings at the Palabora open pit (Surface Mining, 1990)'](image)

The works (Novozhilov, 1972; Yakovlev, 1989) give reasons for the necessity and step of periodic transfer along the height of the haulage level. At the same time, an unsolved problem is to substantiate the rational number of levels being mined simultaneously. The use of several haulage levels can significantly cut the truck transport costs and makes optimisation of their number to be of high priority.

Articulation of objectives

The purpose of the work is to provide a rationale for the design of the transfer point and the opening method with the use of truncated adits, to develop a methodology for optimisation of number and location of IPCC transfer points, at which the costs...
of truck and conveyor transport are minimised. In order to minimise the costs of open pit transport, the case of location of crushing and transfer points on the high wall is considered. In this case, the conveying system consists of two main subsystems:
- delivery of crushed rock from crushing and transfer points to the transfer chamber onto the elevating belt;
- lifting and delivery of rock to the unloading point on the day surface (it is assumed that the entire rock flow from multiple crushing and transfer points is conveyed to the surface by a single elevating belt).
While performing the work, the challenges were dealt with as follows:
- development of a methodology for determining the total costs of truck and conveyor transport;
- study of peculiarities of changes in total costs depending on the parameters of the mining area of the open pit and the number of crushing and transfer points in situ;
- tracing an analytic dependence in order to optimise the number of transfer points provided that they are uniformly located within the limits of the mining area of the open pit.

Presentation of the main study material

Taking into account the peculiarities of opening systems at a number of Ukrainian iron ore open pits (Drizhenko, 2009), it seems possible to consider the option of reconstruction of the transport system of the open pit based on existing permanent underground openings and transfer points on the day surface. Let us consider the common case. The deep levels of the open pit are mined by a system of underground workings (inclined and vertical shafts, an adit) equipped with conveyors and located under the mining pit wall. By the time the decision is made, the immobile crushing and transfer point prevents the advance of mining operations and preserves mineral reserves underneath. The construction of a new immobile crushing and transfer point is irrational, since there is no possibility to make a site of the required size with a lifetime reimbursing the costs of the crushing and transfer point construction. The emergence of this situation is often associated with the mining and geological properties of the deposit, lack of favourable topological features in the deposit structure, which, under the long-term plan, can be used to make sites suitable for placing transfer points with a long service life.

Thus, a vital task is the development of rational process flowchart to open the mining levels using truncated underground workings equipped with conveyors, the development of rational and efficient designs of mobile and semi-mobile transfer points, optimisation of the number, location and capacity of transfer points.

One of the solutions to this problem may be the joint use of a system of conveyors located in adits, mobile conveyors and mobile (semi-mobile) crushers (Novozhilov, 1972; Surface Mining, 1990; Vikul, 2004).

A reasonable option is the use of mobile crushers and a system of mobile conveyors, which transport the rock from the transfer point to the conveyor in the truncated adit. This solution allows continuing the operation of existing equipment and facilities of IPCC and cutting the distance of truck haulage due to the placement of the crusher in the mining area of the open pit.

The process flowchart is proposed as follows: a reloading station for shovels is arranged on a new haulage level (Figure 2). As the equipment of the transfer point, we accept a shovel with a 15-25 m³ capacity bucket, a LT-160 (LT-200) Lokotrack mobile crusher and three or four mobile conveyors, which ensure the mobility of the mobile crusherto relative to the mining front. As the face for shovels moves, we move the mobile crusher and the mobile conveyor system. When the haulage level moves to deeper levels, an inclined conveyor should be added to the process chain in order to connect the mobile group and the conveyor in the underground working. The distinctive features of this technology are: joint use of a system of mobile and semi-mobile conveyors; the use of a transfer point with a mobile crushing plant in the mining area of the deep open pit; shortening the conveyor adit as mining operations advance.

This design of the transfer point ensures the independent operation of truck and conveyor transport, simplifies the arrangement of work to truncate the conveyor adit. The disadvantage of the system is an extra shovel at the transfer point. However, replacing the shovel with a mobile apron feeder will make correlation between truck and conveyor operation rigid.

![Fig. 2. Scheme of mining arrangement at the reloading site for shovels: 1- mobile crusher; 2- mobile conveyors; 3 - semi-mobile conveyor located on the haulage berm](image)

A common disadvantage of most transfer point designs is the need of truck overtravel by one step above the level of the conveyor location. A similar problem is also typical for truck and rail transport (Slobodyanyuk, 2018). A critical analysis of the crushing and transfer point design with the use of a receiving bin to unload the trucks is given by Slepian (1996). It is noted that this design causes a large height of the crushing and transfer point and requires the construction of high retaining walls to hold the loads of trucks. This complicates and raises the costs of the transfer point construction. In addition, the high reloading height leads to excess mileage of trucks. Slepian (1996) proposed a design of the transfer device, which is characterised by operational reliability and reduces excess mileage of trucks. The receiving tank of the crushing and transfer device is made in the form of a bucket. The rear wall of the bucket is separated from it and has the shape of a cylindrical shell. A crusher is located inside the cylindrical shell, and a hole is made in the shell above the inlet of the crusher. The bucket is able to rise by turning around the shell. The transfer device may be equipped with several buckets. Several designs of the crushing and transfer device have been proposed, which differ in the method of unloading the truck into the bucket of the transfer device: without the truck driving into the bucket and with the truck driving into the bucket. The crushing and transfer device operates as follows: the blasted rock is loaded by trucks into the buckets of the crushing and transfer device, which, using hydraulic or rope lifting mechanisms, moves the rock into the crusher inlet. The
crushed rock is loaded from the crusher outlet onto a belt conveyor. Specialists from FLSMIDTH and MAPLESOFT ENGINEERING (Maplesoft, 2015) also came to a similar decision (Figure 3).

Let us consider the possible options for opening systems with truncated underground workings (Vilkul, 2004). The proposed method of opening involves sinking the inclined shafts and adits equipped with conveyors. The adits are located under the mining pitwall. A mobile or semi-mobile transfer point (haulage level) is located near the adit portal. The adits are shortened, the transfer point is relocated as the mining operations advance.

Parallel to the permanent adit is an adit, which is periodically shortened. The permanent adit is equipped with an immobile conveyor, the truncated adit is equipped with a mobile conveyor. The rock in the transfer chamber is reloaded from the mobile conveyor onto the immobile conveyor.

A truncated underground working is equipped with a single transfer unit, and the mobile conveyor is equipped with an intermediate transfer device to reload the rock onto an immobile conveyor. In order to reduce the volume of sinking and capital mining operations, a truncated underground working is sunk as an extension of the adit with an immobile conveyor. Figure 4 shows a fragment of the plan of the mining pitwall with a truncated working, equipped with a single transfer unit.

![Fig. 3. Design of the transfer point proposed by FLSMIDTH](image)

The opening method is applied as follows (Figure 4). An inclined shaft (2), connected with an adit (3), equipped with an immobile conveyor (4) is sunk while mining a steeply dipping ore body (1). The shaft (2) and the adit (3) are located outside the final open pit (11). A truncated adit (5), located parallel to the adit (3) and equipped with a mobile conveyor (6) is sunk from the side of the mining area of the open pit. A mobile crushing plant (7) is installed on the haulage level near the truncated adit portal (5). The transfer unit (8) is equipped with a feeder (9) (chute, vibratory feeder, belt reloader, etc.), which is installed at an angle that ensures reloading the rock from the mobile conveyor (6) onto the immobile conveyor (4). The transfer unit (8) may be equipped with an intermediate transfer device, made, for example, in the form of a diagonal plow (12) or a double-drum unloading carriage.

The pit opening is carried out as follows. The rock is delivered from the mining faces to the mobile transfer point. After crushing, the rock is fed onto a mobile belt conveyor (6). The conveyor (6) transports the rock to the transfer unit (8) and reloads the material by the feeder (9) onto the immobile conveyor (4). When mining operations take place at the truncated adit portal, the mobile conveyor (6) is moved into the depth of the adit (5) by a step of truncation (shown by the dotted line). However, at the same time, the place of reloading the rock from the mobile conveyor (6) onto the immobile conveyor (4) remains unchanged. Whenever blasts are made in dangerous proximity to the conveyor (6), it is moved to the adit (5).

As compared to in-pit crushing and conveying systems being conventional for iron ore open pits in Ukraine based on immobile crushing and transfer points, the traffic patterns using truncated conveyor adits and mobile transfer points have significant technological advantages: the possibility of reducing the truck haulage distance and, as a result, cutting the costs of rock development and the need for dump trucks; high flexibility and mobility of the process flowchart; compactness of equipment; availability to be used on the narrow sites; insignificant restrictions on blasting operations (presplit and low impact blasting at the truncated adit).

![Fig. 4. Option of a truncated adit design](image)

At the majority of iron ore open pits in Ukraine, the rock mass is transported using in-pit crushing and conveying systems (Drizhenko, 2009). As a rule, the process flowcharts that are quite simple in terms of topology with a single immobile crushing and transfer point are used. At the same time, the costs of lifting the rock to the surface are reduced, but the costs of rock delivery by truck to the transfer point remain significant. These costs increase with deeper mining progression and expansion of the mining area. In the mining theory, the issues of substantiating a step of relocating the transfer point in depth while mining operations deepen have been explored, but the issues of the simultaneous use of multiple crushing and transfer points have been insufficiently studied.

Earlier, the authors (Vilkul, 2009) solved the problem of optimising the number of haulage levels in depth of the open pit. With an open pit capacity of 8-20 million tons/year, the use of...
two haulage levels cuts the total costs by 6-22%. With an open pit capacity of 20-30 million tons/year, the use of three haulage levels reduces the total costs by 22-31%. With a capacity of above 40 million tons/year, the optimum number of haulage levels is 4-5, but the major economic benefit is formed when transferring from one to three haulage levels. The utilisation efficiency of multiple transfer points on a single level was also studied by Vilkul (2011). It is shown that using up to three transfer points for a wide range of open pit capacity (10-40 million tons/year) on a single level is reasonable.

This work investigates the features of the simultaneous use of multiple crushing and transfer points, both horizontally and vertically (Figure 5). Let us consider the problem of optimising the number of transfer points (horizontally and vertically), evenly located in the area of mining operations. We divide the area into \( n \) zones horizontally and \( m \) zones vertically. With an increase in the parameters \( n \) and \( m \), the size of separate mining zones and truck transport costs decrease, whereas the operating and capital costs for the rock delivery to the main conveyor using additional (collecting) conveyors increase. The optimum values of the parameters \( n_0 \) and \( m_0 \) are determined from the condition of minimising the total costs of rock delivery from the mining faces to the main conveyor.

Fig. 5. Diagram of dividing the mining area with a height \( H \) into \( m \) zones vertically (\( d_1, d_2, d_3 \) - haulage distances from crushing plants to the main conveyor, m)

The costs of the connecting conveyor system that provide the rock delivery from the crusher to the main elevating conveyor depend on their specific location on the pitwall, as well as on the design features of underground workings in which the elevating conveyor is placed. In this work, the most common, simplified approach is considered, when the haulage distance from each crushing plant to the main conveyor is taken equal to \( d \), \( m \). The required length of the connecting conveyor is determined taking into account the safety of mining operations and the speed of horizontal pushback of the pitwall. Analysis of possible opening methods applied in the open pit mines shows that parameter \( d \) varies within 500-1000 m. This is a simplified model, but at the same time it allows us to determine the main dependences of total costs on the development parameters and optimise the number of transfer points.

The mining area with the size \( L \times H \) (m) and the annual capacity \( Q \) (t/year) is divided into \( n \) zones horizontally and \( m \) zones vertically (total \( n \times m \) zones). The total annual costs of delivering the rock to the main conveyor is

\[
Z = 0.001IQ\left(\frac{C_a + A}{q \cdot T_a} + \frac{H}{4n} + \frac{H}{4mi}\right) + 0.001C_kQ_d + \frac{C_o}{T_k}nmd + \frac{C_d}{T_d}mn,
\]

where \( C_o \) is the cost of truck haulage, USD/tkm; \( A \) is a price of one dump truck, USD; \( q \) is the annual tonnage, tkm/year; \( T_a \) is the rated lifespan of the truck, years; \( i \) is a gradient of haul roads, unit fractions; \( C_c \) is the capital costs per one running meter of additional conveyor workings (taking into account the costs of sinking the adit and of the conveyor), USD/m; \( T_c \) is the period of operation of auxiliary conveyor workings, years; \( C_d \) is the cost of transporting the rock by the conveyor, USD/tkm; \( T_d \) is the period of operation of the crushing and transfer point, years; \( C_d \) is the capital costs per one crushing and transfer point, USD.

The optimum values of the parameters \( n \) and \( m \) are found from the equality to zero of the partial derivatives

\[
\begin{align*}
\frac{n^2m}{T_k} + \frac{C_o}{T_k} + \frac{C_d}{T_d} &= 0.001IQL\left(\frac{C_a + A}{q \cdot T_a} + \frac{H}{4i}\right), \\
\frac{m^2n}{T_k} + \frac{C_o}{T_k} + \frac{C_d}{T_d} &= 0.001IQH\left(\frac{C_a + A}{q \cdot T_a}\right)
\end{align*}
\]

(2)

In order to separate the price and mining-geometrical parameters, we introduce an auxiliary coefficient \( K_t \). Coefficient \( K_t \) is equal to the ratio of unit costs of truck and conveyor transport.

\[
K_t = \frac{0.001IQL\left(\frac{C_a + A}{q \cdot T_a} + \frac{H}{4i}\right)}{4\left(\frac{C_o}{T_k} + \frac{C_d}{T_d}\right)}
\]

(3)

\[
\frac{n^2m}{L} = K_tH
\]

(4)

We divide the second equation by the first one and obtain the ratio between the parameters \( n \) and \( m \), which is determined by height to length ratio of the mining area, as well as a gradient angle of the haul road

\[
m = n\frac{H}{L \times i}
\]

(5)

For the existing mining conditions, we obtain the values of \( m \) two to three times as much as \( n \).

From the first equation of the system (4) we find

\[
n_0 = L\times\left(\frac{K_t}{HL}\right)^{\frac{1}{3}}
\]

(6)

By substituting, we find

\[
m_0 = \frac{H}{i}\times\left(\frac{K_t}{HL}\right)^{\frac{1}{3}}
\]

(7)

The factors under cube roots in formulas (6) and (7) are identical and determine a certain proportionality coefficient for values \( m_0 \) and \( n_0 \). The optimum number of transfer points horizontally \( (m_0) \) is proportional to the length of the mining area, and in height \( (n_0) \), it is proportional to the height of the mining area and inversely proportional to the gradient of haul roads.
Since the performance and mining-geometric parameters in formulas (6) and (7) are under the cube root, even significant changes in one of them lead to a slight change in the optimum number of transfer points. If any of the parameters under the cube root changes by 30%, then \( n_0 \) and \( m_0 \) change only by 9%. Even if one of the initial parameters, for example, capacity, is changed twice, the optimum values of \( n_0 \) and \( m_0 \) will change by 26%.

The total number of transfer points is

\[
m_0 n_0 = \left( \frac{K_i^2 Q^2 L \cdot H}{i} \right)^{\frac{1}{3}}
\]

(8)

We find the optimum distances between transfer points vertically and horizontally

\[
H = \frac{1}{m_0} \left( \frac{H \cdot L \cdot i}{K_1 \cdot Q} \right)^{\frac{1}{3}}
\]

(9)

\[
L = \frac{1}{n_0} \left( \frac{H \cdot L}{K_1 \cdot Q \cdot i} \right)^{\frac{1}{3}}
\]

(10)

We find the vertically projected area of the mining zone per one transfer point

\[
\frac{H \times L}{m_0 n_0} = \left( \frac{H^2 \cdot L^2 \cdot i}{K_1^2 Q^2} \right)^{\frac{1}{3}}
\]

(11)

We find height to length ratio for a particular area

\[
\frac{H}{m_0} + \frac{L}{n_0} = i
\]

(12)

An economic and mathematical model was built on the basis of above formulas and the obtained dependencies. Due to this model, the optimum number of transfer points horizontally and vertically, their total number, the size and area of separate zones, and the capacity of one crushing plant were determined. As the main criterion, the economic benefit was determined \((\Delta Z=Z_n-Z_{min})\) being equal to the difference in total costs of delivering the rock to the main conveyor using a single crushing plant \((Z_n)\) and their optimum number \((Z_{min})\). In addition, the number of trucks for a single and multiple transfer points was determined.

The models were used to study the change in the above parameters when increasing the productivity of mining operations. In this case, the following values of the initial mining-geometric and price indicators were taken into account: height \((H=200 \text{ m})\) and length of the mining area \((L=2000 \text{ m})\); a gradient of the haul road \((i=0.08)\); average distance from the crushing plant to the main conveyor \((d=800 \text{ m})\); truck haulage cost \(C_a=0.2 \text{ USD/km}\); price of a dump truck \(A=\text{USD1.25 million}\); the annual truck tonnage \(q=2.5 \text{ million km/year}\); cost of additional production and installation of auxiliary conveyors \(C_a=\text{USD6.25 thousand/m}\); cost of the crushing plant \(C_c=\text{USD2.50 million}\), the lifespan of auxiliary conveyors and mobile crushing plants \(T=10 \text{ years}\). The simulation results are shown in the graphs (Figures 6-9).

As can be seen from Figure 6, the optimum number of transfer points horizontally \((n_0)\) and vertically \((m_0)\), as well as their total number \((n_0 \times m_0)\), increases with increasing the productivity of mining operations. With a capacity from 13 to 25 million tons/year, it makes sense to use two transfer points placed at different heights, with a capacity from 25 to 55 million tons/year, it is feasible to use four transfer points located on two haulage levels. With a further increase in mining rate, the rational number of haulage levels rises to three (two transfer points at each). The studies show that with an increase in mining rate, the number of haulage levels rises first of all, and then the number of transfer points on the level. The economic benefit (Figure 7) becomes positive with a relatively low productivity of mining operations, and when increasing, both the absolute and the relative value of the economic benefit rises \((100\% \times \Delta Z/Z_n)\).

The use of multiple transfer points makes it possible to reduce the volume of truck operation and the number of trucks twofold to threefold (Figure 8). This explains the significant economic benefits that can be achieved when using multiple transfer points. Cutting the costs of truck transport covers in access the costs of an additional conveyor transport. Apart from a significant economic benefit, this allows simplifying the truck operation in the open pit mine, the haulage length is shortened, the truck traffic is localised in certain areas, and the traffic safety is improved.
The simulation results (Figure 9) show that while using the opening systems with multiple crushing and transfer points, the capacity of the mobile crushing plant varies within 8-12 million tons/year and becomes higher only when the output of the open pit in terms of rock mass is higher than 75 million tons. This conclusion suggests that in most cases, when using the opening systems with multiple transfer points, it will be efficient to use jaw crushers, characterised by a capacity lower than that of gyratory crushers, but requiring significantly lower capital costs. Besides, the crushing and transfer points based on jaw crushers are simpler in terms of design, the mobile and semi-mobile options are acceptable.

**Fig. 8.** Change in the number of dump trucks and their relative reduction while increasing the open pit capacity

**Fig. 9.** Change in the capacity of a single crushing and transfer point and in the distance between the transfer points vertically

**Conclusions and trends for further research**

The research has shown the ability to significantly reduce the costs of truck and conveyor transport using the optimum number of multiple movable crushing and transfer stations. The research results may be used in reconstruction of truck and conveyor transport at the deep open pits. The further research requires substantiating the construction of a movable crushing and transfer station and the methods of mining operations to be used simultaneously in the mining area.

**References**

CALCULATION OF THE MAGNETISING COIL FOR IMPROVING THE MAGNETIC SEPARATION

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ABSTRACT. A coil intended for magnetisation of finely ground magnetite ores during secondary extraction of iron is considered. It is in the shape of a cylindrical ring and is strung on the pulp tube, which is made of non-magnetic and non-conductive material. The coil has known dimensions of the inner diameter and length, obtained for technological reasons. A direct current with a large alternating current component flows through the coil, formed by a diode half-wave rectifier circuit. A methodology is given for determining the electrical parameters of the winding at a given mains supply voltage, heat load and cooling conditions.

Keywords: magnetising coil, magnetic separation, heat load

Introduction

After magnetisation of the ferromagnetic minerals, which are present in ore pulps, relatively stable aggregates are formed, which are a set of particles with residual magnetisation - magnetic flocs. The magnetic floc behaves as a separate, larger magnetic particle until it breaks down. The problem is that the magnetic flocs are formed quite rapidly in the operational area of the separator due to the abrupt introduction of the material under the influence of a strong magnetic field, which is a prerequisite for trapping the slurry particles inside the flocs.

In order to uncover the finely injected useful mineral particles during the secondary extraction of the magnetic iron from the tailings, it is necessary to grind the material, which is a further complication. During the grinding, secondary slurries of non-magnetic and weakly magnetic minerals are formed, which contaminate the flocs. The particles in the pulp with increased coercive properties make it difficult to destroy the magnetic flocs and the purification technological operations are inefficient.

One way to reduce flocs' contamination is to apply preliminary selective magnetic flocculation in separate magnetisers. Their operation must provide conditions for selectivity with respect to the magnetisation of the particles, in the formation of flocs in the suspension’s volume. This is done by gradually increasing the intensity of the magnetic field as the material passes through the operational area of the apparatus. This technological operation must precede the magnetic separation.

Wiring diagram and geometric dimensions of the magnetising coil

A coil of copper conductor is mounted on a non-magnetic and non-conducting pipe, through which a pulp with material subjected to magnetic separation flows (Klisuranov, 1989).

The coil is cylindrical with a rectangular cross section and known dimensions. The inner diameter \( D_1 \), the outer diameter \( D_2 \) and the length \( a \) are set in advance (Figure 1).

The power supply is also set - one-way rectified waved voltage of 400 V (Alexandrov, Savov, 2018) - linear mains voltage without any power matching transformer (Figure 2).

The aim is to create a pulsating magnetic field with a constant and variable component inside the tube, so that the field intensity is maximum at the maximum permissible heat load of the winding.

Fig. 1. Geometric dimensions of the magnetising coil

![Fig. 1. Geometric dimensions of the magnetising coil](image1)

Fig. 2. Simplified wiring diagram for the magnetising coil

![Fig. 2. Simplified wiring diagram for the magnetising coil](image2)

It is necessary to determine the number of turns \( W \), the inductance \( L \), the cross section of the conductor \( S_c \) and the active resistance \( R \), so that the parameters could set the winding in the specified mode.

Defining the inductance \( L \)

Under item 6-5 of a specialized guide (Kalantarov, Zeitlin, 1970) a calculation is made for a round winding with a rectangular cross section (Figure 1).

The geometric dimensions of the winding are calculated:

Mean diameter - equation (1):

\[
d = \frac{D_1 + D_2}{2} = 264 \text{ mm}
\]

Width – equation (2):

\[
a = \frac{D_1 - D_2}{2} = 80 \text{ mm}
\]
\[ r = \frac{D_2 - D_1}{2} = 28 \text{ mm} \]  

(2)

Relation – equation (3):

\[ \rho = \frac{r}{d} = 0.106 \]  

(3)

Relation – equation (4):

\[ \alpha = \frac{a}{d} = 1.019 \]  

(4)

Relation – equation (5):

\[ \gamma = \frac{r}{a} = 0.104 \]  

(5)

According to the proposed methodology (Kalantarov, Zeitlin, 1970) two parallel calculations from different assumptions are chosen for the winding with a rectangular cross-section, which are based on different assumptions.

In order to avoid gross errors, the results of the two calculations are compared. They should give similar results.

The first calculation is based on the inductance of a solenoid according to the expression:

\[ L = \frac{W^2 \cdot \pi \cdot \mu_0 \cdot d}{\alpha} \left( K_\alpha - k \right) \]  

(6)

\[ \mu_0 = 4\pi \cdot 10^{-7} \text{ H/m} \] - magnetic permeability (absolute)

\[ K_\alpha = 0.6928 \] - a factor which depends on \( \alpha \) and is defined according to Kalantarov and Zeitlin (1970) at \( \alpha \) as calculated above.

\[ k = 0.0608 \] - takes into account the end effect factor, depends on \( \rho \) and \( \gamma \), and is determined according to Kalantarov and Zeitlin (1970) at \( \rho \) and \( \gamma \) as calculated above.

\[ L = W^2 \cdot 1.616 \cdot 10^{-7} \text{, H} \]  

(6')

The second calculation is based on the inductance of a flat disk winding according to the expression:

\[ L = \frac{W^2 \cdot \mu_0 \cdot d \cdot \psi \cdot F}{4\pi} \]  

(7)

\[ \psi = 38.92 \] - a factor which depends on \( \rho \) and is defined according to Kalantarov and Zeitlin (1970) at \( \rho \) as calculated above.

\[ F = 0.3088 \] - takes into account the end effect factor, depends on \( \rho \) and \( \gamma \), and is determined according to Kalantarov and Zeitlin (1970) at \( \rho \) and \( \gamma \) as calculated above.

\[ L = W^2 \cdot 1.596 \cdot 10^{-7} \text{, H} \]  

(7')

Both calculations give similar results.

The average value of the two calculations (8) is taken into consideration for our further work.

\[ L = W^2 \cdot 1.606 \cdot 10^{-7} \text{, H} \]  

(8)

### Determination of the impedance modulus

The active resistance \( R \) of the winding is determined according to the expression (9):

\[ R = \rho \frac{\ell}{S_c} \]  

(9)

The length of the conductor is

\[ \ell = \pi d W \]  

(10)

The cross section of the conductor \( S_c \) is determined by the cross section of the winding, the number of turns and the winding space factor \( k \).

\[ S_c = \frac{r \cdot a}{W} \]  

(11)

where \( r \cdot a \) is the winding’s cross section.

Thus, for the active resistance is obtained expression given by (12):

\[ R = W^2 \cdot \rho \frac{\pi d}{k \cdot r \cdot a} \]  

(12)

where:

\[ \rho = 0.017 \cdot 10^{-6}, \Omega \frac{m^2}{m} \]  

\[ R = \frac{W^2}{k} \cdot 1.87 \cdot 10^{-6}, \Omega \]  

(12')

It is assumed \( k = 0.9 \) for a profile conductor with a rectangular cross section.

\[ R = W^2 \cdot 2.08 \cdot 10^{-6}, \Omega \]  

(12'')

It is evident that the active resistance \( R \) (12'') as well as the inductance \( L \) (7) are proportional to the square of the number of turns \( W^2 \).

The inductive resistance \( X_L \) is

\[ X_L = \omega L \]  

(13)

\[ X_L = W^2 \cdot 314.1,606 \cdot 10^{-7} = W^2 \cdot 50.43 \cdot 10^{-6}, \Omega \]  

(13')

\( \varphi \) is determined from the triangle of impedance by

\[ \tan \varphi = \frac{X_L}{R} = \frac{W^2 \cdot 50.43 \cdot 10^{-6}}{W^2 \cdot 2.08 \cdot 10^{-6}} = 24.24 \]  

(14)

\[ \varphi = \arctg 24.24 \approx 87.6^\circ = 1.53 \text{ rad} \]  

(15)

It does not depend on \( W \).

Reading from tables for the intermediate values of the argument (Kalantarov, Zeitlin 1970) is done by interpolations.

The modulus of impedance is

\[ Z = \sqrt{R^2 + X_L^2} \]  

(16)
Determining the instantaneous value of the current through the winding

This current consists of a series of pulses, the pulse starting at the moment of opening the diode $t_0$ and ending at the moment of blocking the diode $t_1$. At purely active load $t_1 = T/2$, at active-inductive load $t_1 > T/2$ where $T$ is the grid period.

The current is determined as a transient process with two components (sinusoidal and exponential), as follows from (17):

$$i(t) = i_{\sin} + i_{\exp}$$

The constant $A$ is defined for $t = 0$.

$$i(0) = I_m \sin(-\varphi) + A = 0, \quad A = I_m \sin \varphi$$

where $I_m$ is maximum value of the current through the winding.

Let the moment at which the diode is blocked and the current becomes zero be $t_1$. Then

$$\sin(\alpha t_1 - \varphi) = -\sin \varphi e^{-\frac{t_1}{\tau}}$$

where $\varphi = 87.6^\circ = 1.53$ rad

$$\sin \varphi = 0.999 = 1$$

$$\tau = \frac{L}{R} = \frac{W^2 \cdot 1.606 \cdot 10^{-7}}{W^2 \cdot 2.08 \cdot 10^{-6}} = 0.0772$$

The time constant $\tau$, does not depend on $W$.

After substituting the numerical values in (21) for a grid with frequency of 50 Hz, we get:

$$\sin(100\pi t_1 - 1.53) = -e^{-12.95 t_1}$$

The sine function and the exponential function are graphically presented (Figure 3) and their intersection point, which corresponds to $t_1$ between 0.8$T$ and 0.9$T$, is determined.

For example, for $t_1 = 0.89 - T$ the functions acquire the following values:

$$\sin(100\pi t_1 - 1.53) = -0.796$$

$$-e^{-12.95 t_1} = -0.794$$

which are very similar.

It is assumed that the diode is blocked at a time

$$t_1 = 0.89 - T = 0.89 - 0.02 = 0.078 \text{ s.}$$

Defining the effective value of the current

The effective value of the current can be presented by:

$$I^2 = I_{ac}^2 + I_{dc}^2$$

$$I^2 = \frac{L}{T} \int_0^{t_1} \sin^2(\alpha t - \varphi) \, dt + \frac{L}{T} \int_0^{t_1} e^{-\frac{t}{\tau}} \, dt$$

The solution of the two defined integrals is:

$$I^2 = \frac{I_m}{T} \left[ \frac{1}{4\alpha} \sin(2\alpha t_1 - 2\varphi) \cdot \frac{1}{2} e^{2\alpha t_1} + \frac{1}{2\alpha} \sin 2\varphi \cdot e^{2\alpha t_1} \cdot \frac{1}{2} \right]$$

$$= \frac{I_m}{T} \left[ \frac{1}{4\alpha} \sin(2\alpha t_1 - 2\varphi) + \frac{1}{4\alpha} \sin 2\varphi \cdot \frac{1}{2} e^{2\alpha t_1} + \frac{1}{2\alpha} \sin 2\varphi \cdot \frac{1}{2} e^{2\alpha t_1} \cdot \frac{1}{2} \right]$$

After substituting the above values of (20), (26), (22), $\varphi = 1.53$ rad, $\omega = 314$ rad/s and $T = 0.02$ s in (29) we obtain

$$I^2 = I_{dc}^2, 1.1155$$

where $I$ – effective value of the current which has a constant and a variable component, $I_m$ - maximum value of the variable component.

Correspondingly, the effective value of the current $I$, is

$$I = 11.88 \cdot 10^6 / W^2, \text{ A.}$$
Determination of the number of turns $W$ according to the heat load of the winding

Defining the surface of the winding $S_{wind}$

$$S_{wind} = \pi (D_1 + D_2) + 2\pi r_a = \pi (236 + 292) + 2\pi 264.28 = 492630 \text{ mm}^2 = 4926 \text{ cm}^2$$  \hspace{1cm} (32)

Defining the active power of the winding $P$

The active power of the winding $P$ is calculated according to the equation (33) where $I$ – effective current value (31) and $R$ – active resistance of the winding (12"):

$$P = I^2 R = \left( \frac{11.88 \times 10^6}{W^2} \right)^2 \cdot W^2 \cdot 2.08 \times 10^{-6}$$

So the surface of the winding is $S_{wind} = 4962 \text{ cm}^2$ and the active power is

$$P = \frac{1}{W^2} \cdot 293.6 \times 10^6 \cdot W$$  \hspace{1cm} (34).  

The number of turns $W$ should be determined so that the surface of the winding is able to emit this power in the surrounding atmosphere primarily through convection. We calculate how many watts are emitted per square centimetre ($\sigma$):

$$\sigma = \frac{P}{S_{wind}} = \frac{293.6 \times 10^6}{W^2 \cdot 4926} = \frac{59600}{W^2} \cdot \frac{W}{\text{ cm}^2}$$  \hspace{1cm} (34)

The convection cooling depends on the air temperature and the air circulation that blows and cools the coil.
The value of $\sigma$ is determined experimentally by a reduced home-made physical model of the winding so that the surface temperature does not exceed 70°C at temperature of the air of 20°C. The following expression is used to define the number of turns obtained by rearranging (34)

$$W = \sqrt{59600/\sigma}$$  \hspace{1cm} (36)

Experimentally obtained values of $\sigma$ at the permissible temperature of the winding surface, which are used to determine $W$ are presented in Table 1.

<table>
<thead>
<tr>
<th>$\sigma$, $\text{W/cm}^2$</th>
<th>$W$, turns</th>
<th>Cooling conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.09</td>
<td>814</td>
<td>At better cooling conditions</td>
</tr>
<tr>
<td>0.08</td>
<td>863</td>
<td></td>
</tr>
<tr>
<td>0.07</td>
<td>923</td>
<td>At worse cooling conditions</td>
</tr>
</tbody>
</table>

Defining the cross-section of the conductor

After determining the number of turns for the respective cooling conditions, the cross section of the conductor can be found according to formula (11) to give:

$$S_c = \frac{k a}{W} = \frac{28.269}{W} = \frac{6779}{W}, \text{ mm}^2$$  \hspace{1cm} (37)

Defining the magnetomotive force - m.m.f.

To assess the possibilities for creating a magnetic flux and, accordingly, for the magnetisation of the material in the working volume of the device, the m.m.f. is found by dependence (38).

$$F = W \cdot I \cdot A$$  \hspace{1cm} (38)

After substituting the current from (31) in (38) the following is obtained for m.m.f.:

$$F = W \cdot \frac{11.88 \times 10^6}{W^2} = \frac{11.88 \times 10^6}{W^2} \cdot A$$  \hspace{1cm} (39)

For the corresponding number of turns from Table 1 the following values of m.m.f. are obtained.

At $W = 814; \quad S_c = 8.33 \text{ mm}^2; \quad F = 14.6 \text{ kA}$.
At $W = 863; \quad S_c = 7.85 \text{ mm}^2; \quad F = 13.8 \text{ kA}$.
At $W = 923; \quad S_c = 7.34 \text{ mm}^2; \quad F = 12.9 \text{ kA}$.

It is evident that at a greater heat load ($I = 0.09; W = 814$) m.m.f. is 14.6 kA and at a lesser ($I = 0.07; W = 923$), m.m.f. is 12.9 kA, values which can create a magnetic field with enough intensity for the magnetisation of the material which is in the range from 32 kA/m to 40 kA/m (Klisuranov, 1989).

**Conclusion**

The number of turns and the cross-section of the conductor of the magnetising coil are defined so that the induction in the pipe is the maximum at the permissible heat load.

On the basis of the presented calculation, an experimental device with a magnetising coil and a power electronic power supply unit has been designed. The manufactured coil is shown on Figure 4.

![Fig. 4. The magnetising coil](image)

**References:**


