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VALORIZATION OF USEFUL COMPONENTS FROM THE SEDEX TYPE ORE THROUGH THE HORIZON 2020 "INTMET" PROJECT

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Abstract

Europe is heavily dependent on imports the raw materials (RM) and needs to increase a domestic supply to ensure the global competitiveness of its manufacturing industries and accelerate the transition to a resource-efficient, sustainable society. Demand for resources will increase due to the global population growth, industrialization, digitalization, growing demand from developing countries and transition to the climate neutrality with metals, minerals and biotic materials, used in the CO_2 low-emission technologies and products. The RMs are essential for the EU industry and are at the core of every value chain. Among them, the critical raw materials (CRM) are often produced and used in relatively small quantities, but have the unique characteristics that make them essential ingredients for products in the strategic areas such as the renewable energy, digital, aerospace and defense technologies. To strengthen the EU's open strategic autonomy, the Critical Raw Materials Act will soon be published in 2024 to ensure an access to the secure, resilient and sustainable CRM supply, fostering efficiency and circularity throughout the value chain. Several decades of absence of the Mineral Raw Materials (MRM) policy in the EU and most EU member states has led to a significant lack of knowledge about the MRM. Technological solutions of a sustainable green energy play a key role especially for application the newly discovered materials. Potential additional sources of the CRM certainly represent the SEDEX type of ore materials. The EU updates the CRM list every year according to the market needs, and the SEDEX ore type contains metals that have been on that list for years. The SEDEX type of polymetallic ore presents a new challenge considering that it contains components that are more valuable. They contain valuable critical metals (Cu, Zn, Pb, Au and Ag). Within this project title Integrated Innovative Metallurgical System to Benefit Efficiently Polymetallic, Complex and Low-Grade Ore and Concentrates under the acronym the "IntMet", the new technologies were developed for obtaining all valuable metals from this very complex mineral resource that cannot be treated in an economically and environmentally acceptable way with the conventional technologies (flotation, pyrometallurgy, etc.).

Keywords: *Critical Raw Materials, new metallurgical system, Sedex ore, bioleaching*

1. INTRODUCTION

Europe possesses the natural resources, and extraction and supply of the mineral resources continues to play a key role in the European economy and society. Considering the degree of development of the EU economy, its needs are far greater than its own possibilities of supplying the domestic mineral raw materials.

Extending the life of existing mines is reflected in the possibility of exploitation the completely new unused (off-balance low-content resources or difficult-to-valorize resources), e.g. SEDEX type of ore.

The study of technological treatment procedures and finding the possibility of processing, the non-standard polymetallic raw minerals with a high and low content of metals Cu, Zn, Pb, Au, Ag, SEDEX-type ore and tailings from active and abandoned mines, has become the interest of many authors.

It is not possible to treat the SEDEX raw materials with conventional flotation and pyrometallurgical technologies because they are used for the standard forms of ore mineralization, which is not the case with the subject ore that was treated in the project [1]. In the world, more and more researchers are working on development the selective hydrometallurgical processes in order to valorize all useful metals.

In Serbia, the polymetallic off-balance ore containing copper, zinc, lead, gold and silver is found in quantities that meet and even exceed the country needs. The polymetallic sulphide ore deposits are located in Western Serbia - Bobija, Majdan, Central Serbia - Rudnik Mine and Eastern Serbia - Čoka Marin, Tenka, Southern Serbia - Grot, Lece. These polymetallic deposits consist of the ore bodies with different morphological and structural textural specific characteristics related to the different location areas.

Polymetallic paragenesis is mainly formed from sulfides with a dominant pyrite content. This polymetallic ore contains lead, zinc and copper with an added mixture of arsenic, antimony, gold, silver, bismuth, calcium minerals and barite. The analysis of massive samples of sulphide ores showed a high content of base metals (>10% Zn and Pb) as well as the content of precious metals.

The IntMet project has a certain approach and represents a radical solution and unique technological discovery to definitively overcome the limitations related to heavy, low-quality and complex ore in order to achieve a high-efficiency recovery of valuable metals such as Cu, Zn, Pb, Ag and Au. In addition, the secondary materials such as tailings and metallurgical waste are also treated in the aim of metal valorization and recovery. Technical, environmental and economic feasibility are integrated units that offer a realistic technological economic solution. The ultimate goal was to ensure the economic viability of the entire IntMet project.

Several technological solutions have been proposed in the project, such as the atmospheric leaching, pressure leaching and bioleaching. The task of the Mining and Metallurgical Institute Bor was the application of bioleaching for the treatment of SEDEX type ore from the Bobija site in Western Serbia.

2. EXPERIMENTAL

The amount of off-balance ore reserves of Serbia containing Pb and Zn is estimated at about 47 million tons with a content of 1.92 wt% Pb and 1.12 wt% Zn [2,3]. In the domain of lead-zinc ore exploitation in Serbia, the following mines are active: Veliki Majdan, (company Mineco Ltd); Mine Rudnik (company Contango); Kiževak-Sastavci (company Farmakom); Grot (majority of the capital is the socially-owned). Yearly production is about 800.000 tons of Pb-Zn ore. Due to the change of ownership, the polymetallic deposits of eastern Serbia in the territory of the municipality of Majdanpek – North Mining District, Tenka, Dolovi, Čoka Marin, which belonged to RTB Bor, are now the property of the Chinese company ZiDjin Mining doo. The Grot and Lece also belong to the polymetallic deposits. The Bobija-Ljubovija deposit is the SEDEX ore type. Figure 1 presents the locations of all these polymetallic types of ore sites. For all this type of ore is very important to find the appropriate BAT technology (Best Available Technology), which will then be

applied. The main goal is the valorization and increasing of extraction of all useful metals from the raw materials, which today are difficult to treat with the conventional technologies.

Figure 1. *Polymetallic ore type in Serbia*

2.1 SEDEX Type Ore from Western Serbia – Bobija Treated on the IntMet Project

For research on the accepted European IntMet project under the program package of the Horizon 2020, the Bobija ore from Western Serbia was selected. This ore is very compact with no visible mineral formations and minerals are highly impregnated into the basic rock mass. The expected reserves for the polymetallic deposit Bobija, at the then the level of research were estimated at 4-6 million tons with metal content: 0.75 – 1.5 % Cu, 3.5 – 4% Pb, 4.5 – 6% Zn, 1.5 g/t Au, 120 – 150g/t Ag, 15 – 30% $BaSO_4$.

It was determined by the mineral microscopic testing that a complex mineral association occurs in the polymetallic mineralization, comprising the following minerals: sulphides (pyrite, sphalerite, wurtzite, galena, arsenopyrite, marcasite, pyrrhotite, chalcopyrite, covellite, chalcocite), sulphosalts (tetrahedrite - tennantite), metals (native silver), non-metallic minerals (barite), and waste minerals (quartz, chalcedony, carbonates, azurite, malachite, anglesite, cerussite, smithsonite).

The content of sulphide mass in the whole sample was 63.6%. Figure 2 shows the percentage ratio of sulphide, barite and waste minerals in sample which are calculated

to100% of sulphide minerals. The most represented sulphide mineral in sample is pyrite. Figure 3 shows the percentage participation of sulphide minerals in sample.

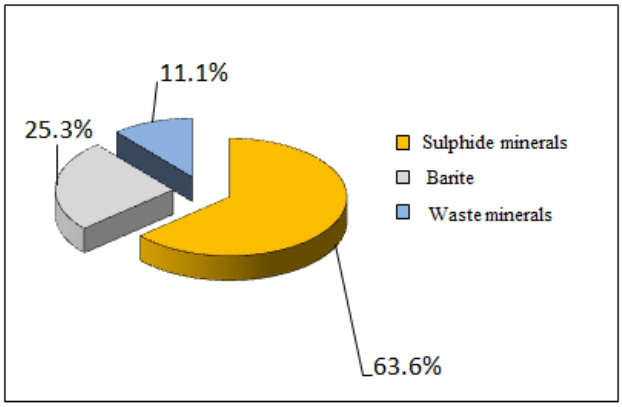


Figure 2. *Percentage ratio of sulphide, barite and waste minerals*

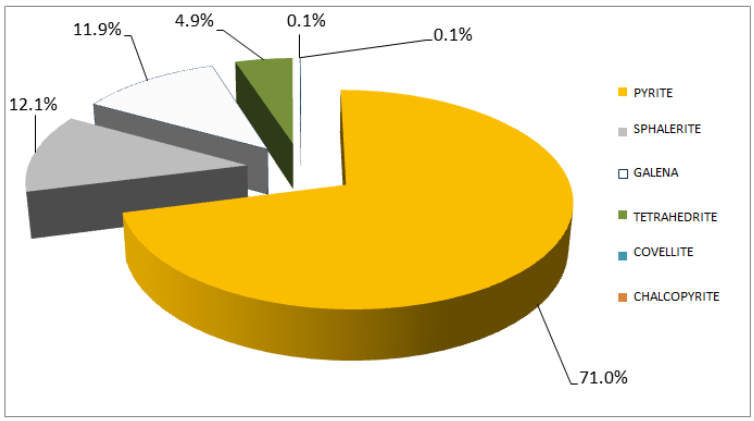


Figure 3. *Percentage participation of sulphide minerals*

It can be concluded from research results that it is not possible to enrich the ore to obtain any selective or collective sulphide concentrate using the conventional mineral processing methods (flotation concentration), and that it is necessary to include the new technological procedures for the ore processing. In addition, a review of the literature determined that valorisation of useful components by the classical procedures of flotation the lead-zinc ore of Bobija is not possible because the low-grade concentrates with the low recovery are obtained [4]. This is also the suggestion of other authors [5]. Reviewing of this literature, a proposal for a new technology for valorization the useful metals was given. Namely, the given proposal involves the roasting to convert BaSO4 into BaS, which is easily soluble in water. In this way, iron in the form of pyrrhotite can be removed by a magnetic separation. Leaching of Zn and Cu with sulfuric acid gives a high leaching rate and by this way lead remains in a solid residue, which can be further treated with the lead concentrates.

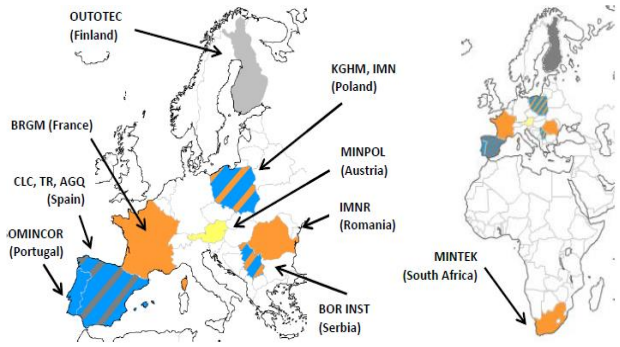
Although good results are achieved in terms of quality and metal recovery, the technology is questionable from an economic point of view, because the process involves roasting, which often has no economic and environmental justification.

In this way, the possibility of treating these types of raw materials with the bioleaching processes, which overcome the mentioned difficulties in obtaining the high-quality metals, is opened. It can be concluded from the mineralogical characterization that there is a justification for treatment of this raw material with a high content of useful metals, especially pyrite, with the proposed biotechnology.

2.2 The Basic INTENT Project Details

The basic details of the INTMET project are presented in Table 1.

Table 1. *The basic details of the INTMET project*

Project Title:	Integrated innovative metallurgical system to benefit efficiently polymetallic, complex and low grade ore and concentrates.
Acronym:	INTMET
Project number:	689515
Topic call:	SC5-11e-2015 New metallurgical systems
Duration in month:	36
Participants:	
Total project value:	7834976.25€
Project manager for MMI Bor participations:	PhD Dragan Milanović, BSc.mineral processing
Project team for MMI Bor participations:	PhD Vlastimir Trujić, B. Eng.metall. PhD Mile Bugarin, B. Eng. geol. PhD Vesna Conić, B. Eng.metall.
MMI Bor	Contibutor in WP5- Bioleaching

2.3 Equipment Obtained by Participation in the Project

The application of biotechnology in the IntMet project showed a major technological breakthrough in obtaining metals Cu, Zn, Pb, Au and Ag from the polymetallic mineral raw minerals from the open pit Bobija, Ljubovija - Western Serbia.

Bioleaching was carried out at 30^0C in the presence of adapted mesophilic mixed bacterial culture containing *At. ferrooxidans, At. thiooxidans, and L. ferrooxidans*, with the addition of heterotrophic acidophilic culture *Acidifilium cryptum* presented in Figure 4.

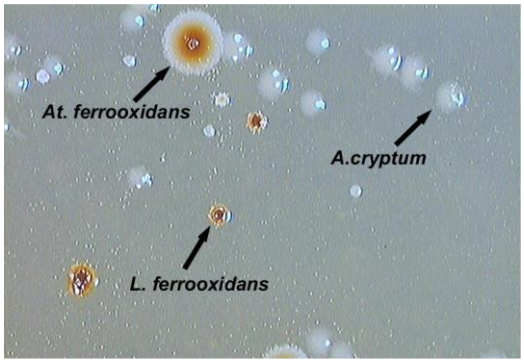


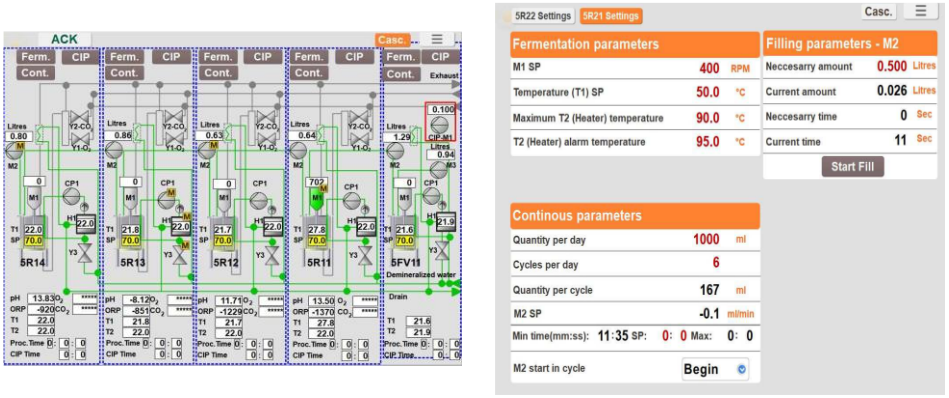
Figure 4. *Colonies of acidophilic bacteria (S. Stanković, 2016)*

After adapting the microbiological culture to 5%, 7%, 10% and 15% (v/w) pulp density, the bioleaching tests were performed in the continuous bioreactor systems. These systems were developed in cooperation with the IntMet participant responsible also for the implementation of the WP5 MINTEK Institute from South Africa and in cooperation with the Biotech Company from Latvia that constructed the equipment. The equipment contains a high level of control and automation of all operating parameters with the usage of SCADA software. Two continuous bioleaching lines of different capacity were made, a small continuous bioleaching line with a capacity of 1L/day pulp Figure 5a, and large continuous bioleaching line with a capacity of 20L/day pulp Figure 5b. For both lines, the electrical supply installations, tap water, demineralized water, CO_2 gas, air, exhaust installation and sewerage are provided. A system for measuring and controlling the concentration of CO_2 and O_2 in the exit gases is also provided.

a) **b)**

Figure 5. *a) Small glass laboratory scale bioreactors for continuous bioleaching of the ore with a capacity of 1 liter pulp/day; b) Large scale bioreactors for continuous bioleaching of the ore with a capacity of 20 liter pulp/day*

The SCADA software with the main control panel window with the reactor settings, presented in Figure 6, facilitated the daily monitoring of the bioleaching process in order to control the pH value, redox potential, pulp flow in bioreactor systems, constancy in the process temperature and pulp mixing speed, controlled supply of O_2 and CO_2 gases.



(a) (b)

Figure 6. *a) Main control panel window; b) Reactor settings*

Adapting the microbes to the mineral raw material and establishing the continuous bioleaching in a series of bioreactors after determining the retention time (cumulative time that the mineral ore spends in the bioreactor systems after addition), it is possible to continuously obtain a leached pulp. After filtration the leached pulp, the leaching solution and solid residue are obtained. The leaching solution contained Cu, Zn and Fe. The solid residue contained Pb, Ag and Au, which were further treated by the chemical leaching to valorize it.

3. RESULTS AND DISCUSSION

3.1 Project Results

The obtained project results were presented at the Internationa Mineral Processing Conference IMPC 2018 in Moscow with a detail showing. The proposed technological scheme of processing and valorization of popularly called the big five metals is presented in Figure 7. Valorization of metals Cu, Zn, Pb, Au and Ag resulted in the high recoveries of all metals, 83%, 89%, 90%, 90% and 80%, respectively. The qualities of obtained products were of the following purity: Cu cathode – 99.99%, Zn cathode – 99.99%, Pb cathode – 99.95%, Au powder – 99.90% Au, Ag powder – 99.80%.

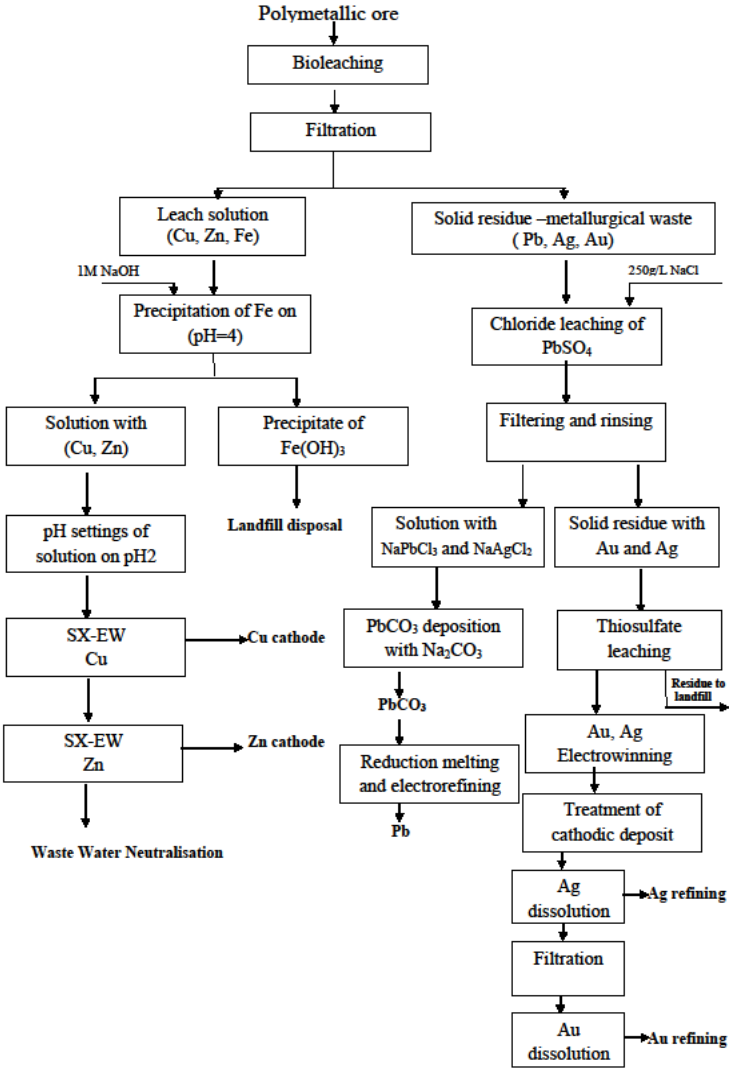


Figure 7. *Technological scheme of processing the polymetallic SEDEX type ore Bobija*

4. CONCLUSION

The Serbian Mining has a good base for further development, which reflects both raw materials and t skilled personnel and extensive professional experience.

- Newly discovered deposits and potentials provide the perspective for development and reaching of 3% of participation of the mining industry in the Brutto Social Revenue.

- In order to keep a stable supply of market with all kinds of mineral resources, mining will be developed in accordance with the requirements of modern society in terms of the technological advances, economic and environmental sustainability, which is fully in accordance with the proclaimed principle, contributing to the achievement of all goals the EU, EIT Row materials under the umbrella Knowledge and Innovation Community – KIC.
- In this approach, the technology for treatment the extremely difficult raw materials SEDEX type is presented. In addition, the proposed technology is very suitable for valorization the useful metals from all sulphide polymetallic raw materials.
- The advantages of this technology are reflected in:
  - High recoveries of useful metals from the SEDEX type ore Bobija: 83% Cu%, 89 Zn%, 90% Pb, 90% Au and 80% Ag with the high product qualities: Cu cathode – 99.99%, Zn cathode – 99.99%, Pb cathode – 99.95%, Au powder – 99.90% Au, Ag powder – 99.80%,
  - Flexibility in terms of capacity because it can be installed on a modular basis and therefore can follow variations in the production capacity of the mine by the simply raising more production modules,
  - Possibilities of easier treatment the previous flotation phase in terms of establishing a collective flotation concentration of all sulphide minerals, including pyrite, which avoids a complex flotation process of selective flotation with various benefits (simpler technological scheme of the flotation process with a reduction in the number of working machines, labor force, consumption of normative, etc.,
  - Biotechnology is an integral part of sustainable metallurgical systems (mining, flotation, bio, hydro, ion extraction, SX-EW, etc.),
  - Environmental protection with minimizing the environmental footprint,
  - The ability of this technology to treat the low-content raw materials unlock a substantial volume of the polymetallic raw materials for exploitation in the ESEE Region.

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