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PRESENTATION OF THE FP6 EUROPEAN PROJECT BIOSHALE: EXPLOITATION OF BLACK SHALE ORES USING BIOTECHNOLOGIES - POLISH CASE STUDIES

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The Bioshale project, involving 13 partners throughout Europe, is co-funded by the European Commission under the FP6 program. The main objective of this project (which started in October 2004) is to identify and develop innovative biotechnological processes for "eco-efficient" exploitation of metal-rich, black shale ores. Three extensive deposits have been selected for R&D actions. These are: (i) a site (in Talvivaara, Finland) that, at the outset of the project, had not been exploited; (ii) a deposit (in Lubin, Poland) that is currently being actively mined, and (iii) a third site (in Mansfeld, Germany) where the ore had been actively mined in the past, but which is no longer exploited. The black shale ores contain base (e.g. copper and nickel), precious (principally silver) and PGM metals, but also high contents of organic matter that potentially handicap metal recovery by conventional techniques.

The main technical aspects of the work plan can be summarized as: (i) evaluation of the geological resources and selection of metal-bearing components; (ii) selection of biological consortia to be tested; (iii) assessment of bioprocessing routes, including hydrometallurgical processing; (iv) techno-economic evaluation of new processes from mining to metal recovery including social, and (v) assessing the environmental impacts of biotechnological compared to conventional processing of the ores. An overview of the main results obtained to date are presented, with special emphasis on the development of bioleaching technologies for metal recovery that can be applied to multi-element concentrates and black shale ores from Poland.

Key words: bioleaching, biotechnology, mineral processing

INTRODUCTION

The natural ability of microbes to degrade minerals was already used in the Roman times for copper recovery, without awareness of the role of micro-organisms. In the last 30 years, extensive research has been carried out on biooxidation and bioleaching

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processes. As a consequence, and where circumstances are favourable, biohydrometallurgy emerged as an industrial reality and a alternative for the treatment of some minerals (sulphides, oxides) and the recovery of metals such as copper, gold and cobalt (Rawlings and Johnson, 2007). There could be applications of "biomining" technologies for the recovery of other metals, such as rare and precious metals (PGM), or for processing other type of mineral targets, such as black shale ores but these would need significant technical and scientific engineering advances.

Since 2004, two consortia of industrial and research organisations, supported by the European Commission in the Sixth Framework Programme for Research and Development, have attempted to contribute to the transformation of the mineral industry towards cleaner, safer and more environmentally friendly production methods. These projects are BIOSHALE, a targeted project that aims at developing the potential of biotechnology for exploitation of "black shale - Kupferschiefer" ores for base and rare metals production, and BioMinE, a large integrated project that will allow the integration of innovative biotechnology based processes for recovery or removal of metals from primary European resources (ores and concentrates) and secondary materials (Morin et al., 2006).

All aspects concerning this project, including the Finish case study and the main results were recently presented at the Minerals Engineering conference that was held in Falmouth, UK in May 2007 (d'Hugues et al., 2007). This paper presents an overview of Bioshale project, with a special emphasis on both the biotechnological aspects of the project and the Polish case studies.

CONTEXT AND GENERAL DESCRIPTION OF THE PROJECT

European deposits of black shale ores contain considerable reserves of base and highly valuable rare and precious metals (including Cu, Ni, Zn, Pb, Ag, Zn, Co, Au, Pt, Pd), of which Europe is a main consumer. The black shale ores are typically poly-metallic ores with a variable proportion of sulphide components. In particular, the "Kupferschiefer" is a lithological formation that extends over 600,000 km² from England to Poland, but of which exploitable Cu reserves represent only 0.2% of the total area, notably at the southern edge of the Zechstein Basin. To date, more than two million tons of copper have been produced from this geological formation, along with noble and rare metals, extracted as by-products but often with a poor recovery. In Poland, the Lubin ore deposit which is currently being exploited belongs to this type of geological formation and evaluation of potentially more efficient and environmentally sensitive processing routes is of strategic importance for the Polish copper industry. In Finland at Talvivaara, the potential exploitation of a large, low-grade black shale ore deposit containing Ni, Cu and Zn was under evaluation when the Bioshale project started. The Mansfeld/Harz site in Germany has large amounts of black shale ore residues resulting from many years of mining activities in the area.

These three sites, at three different stages of development, were targeted to support the studies of innovative ways of processing black shale ores. Two major difficulties restrict the exploitation of such abundant resources. The first is the low efficiency of the conventional technical means for recovering valuable metals, from mining extraction to metallurgical processing. The second is the environmental impact of the application of the conventional techniques, even with the goodwill of the mining and metallurgy industries on this matter. From the processing point of view the black shale ores have specific features within a variable morphology: the metal-bearing compounds are dispersed as small-size particles and the valuable metals may be trapped in organic matter in the ore or in slimes. This explains the limited recovery of the metals and the problems encountered in the processing and management of the tailings.

The research and development challenge in this respect is two-fold. The first is to transpose the existing know-how in the treatment of sulphidic ores to black shale ores, and the second is to investigate new processing ways for beneficiation of the shales, among which could be the biotreatment of the organic components and the use of bioflotation for improving the production of concentrates. Therefore, natural biological activity in ore deposits and mining wastes stockpiles has been screened in a search for new bioprocessing reagents and in order to assess its influence on the environmental impact of the present and future mining activities.

OVERVIEW AND OBJECTIVES OF THE BIOSHALE PROJECT

“Bioshale” is a Specific Targeted Research Project co-funded by the European Commission in the frame of the FP6 programme (contract - NMP2 - CT - 2004 505 710), with a total budget of 3.4 M€ (EC contribution 2.3 M€).

The project duration is 3 years, and it began on 1st October 2004. In order to take up the scientific and technical challenges of the project, a multidisciplinary partnership (Table 1), working complementarily on the different case studies was implemented. The work was broken down in 6 Work packages-WP (Fig. 1).

The main goal of the Bioshale project is to define an innovative biotechnological processes for the “eco-efficient” exploitation of black shale ores for metals production. The main tasks involved are : (i) evaluation of the geological resources (geological modelling); (ii) selection of metal-bearing materials and biological consortia to be tested; (iii) assessment of bioprocessing methods and determination of complementary hydrometallurgical processing routes for metals recovery; (iv) risk assessment relative to wastes management of the new processing routes; (v) techno-economic evaluation of new processes from mining to metal recovery, including social and environmental impacts.

Three large-scale black shale deposits, of various stages of exploitation, were selected at the outset of the project. There were:

- (i) an un-mined deposit, located in Talvivaara, Finland;

- (ii) a deposit that is actively mined (and which accounts for the largest point production of copper in Europe) located at Lubin, Poland,
- (iii) and a post-mining deposit (Mansfeld, Germany). The social and economic benefits of this project aim to extend the exploitation life of European mining sites in operation (Lubin) and to allow exploitation of new resources with considerable reserves (Talvivaara). The site of Mansfeld in Germany was chosen to illustrate and support the evaluation of the Environmental Impact of exploiting black shale ores.

Table 1. Description of the Bioshale consortium

Participant Name	Country	Role
Bureau de Recherches Géologiques et Minières	France	Project coordination / WP5 leader - R&D activities in microbiology, biotechnology, geology, mineralogy & socio-economy
KGHM CUPRUM sp. z o.o. CBR	Poland	WP2 leader- Topic leader (technology/Engineering) R&D activities in geology, mineral processing and environmental impacts - sample provider
Wroclaw University of Technology	Poland	R&D activities in mineral processing, biotechnology and hydrometallurgy
University of Opole	Poland	R&D activities in microbiology & mineral processing
University of Warsaw – Faculty of Biology - CEMERA	Poland	Topic leader (environmental impacts) - R&D activities in microbiology, biotechnology & environmental impacts
Geological Survey of Finland	Finland	WP6 leader - R&D activities in mineral processing, biotechnology, mineralogy, environmental impacts & socio-economy - sample provider
Helsinki University of Technology	Finland	R&D activities in geology, mineralogy, electrochemistry & environmental impact
Técnicas Reunidas	Spain	WP4 – leader - R&D activities in mineral processing, hydrometallurgy and socio-economy
University of Wales, Bangor	UK	WP3 leader - R&D activities in microbiology and biotechnology
University of Warwick, Biological Science	UK	Topic leader (microbiology) - R&D activities in microbiology and biotechnology.
G.E.O.S. Freiberg, Ingenieurgesellschaft mbH	Germany	R&D activities in geology & environmental impacts
University of Mining and Geology “Saint Ivan Rilski”, Sofia	Bulgaria	R&D activities in mineral processing, microbiology, biotechnology and environmental impacts
Czech Geological Survey	Czech Republic	R&D activities in geology & mineralogy

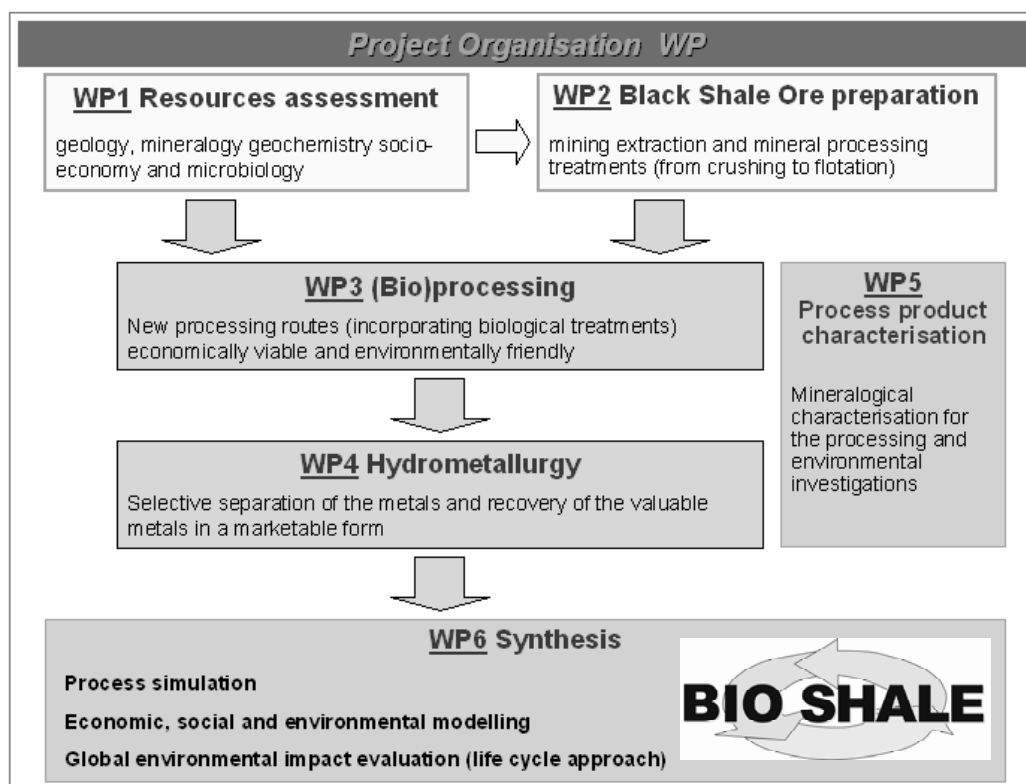


Fig. 1. Overview of the Bioshale project structure

BIOHYDROMETALLURGY AS A POTENTIAL OPTION

In order to evaluate the potentiality of bioprocess alternatives, regarding technical, environmental and economic criteria, a global analysis was carried out to better understand the real position of bio-technologies in comparison with alternative ones. This general study was mainly focused on copper of which production is ensured through a large variety of processes.

In biohydrometallurgy, two types of techniques exist and are proved as being reasonable technical and industrial options. The first one, and most simple, is the bioheap leaching technology. The crushed ore or the agglomerated concentrate/ore is placed in heaps and irrigated. The pregnant solution obtained by percolation through the heap is either recycled or used for downstream processing steps and metal recovery by hydrometallurgical routes. This technology is mainly applied for the treatment of copper ores. Some operation for pre-treatment of gold-bearing ores were also implemented. There are currently several bioheap-leach operations world-wide processing copper sulphide ores (Rawlings et al, 2003; Watlings, 2006). Two among them are treating primary sulphide (chalcopyrite) ore at pilot scale. Many bioheap

processes have targeted extraction of marginal ores not suitable for concentration and smelting.

The main operators are: Newmont Mining, Phelps Dodge, BHP Billiton, RioTinto, Mintek, and Codelco. The critical reasons for selecting bioheap over other techniques can be summarised as follows:

- low capital and operating cost, easy to operate, mainly inert wastes
- flexible in size, remoteness of the mine and cost for transportation
- less sensitive to impurities in the feed material (“dirty” concentrates with high impurities levels are charged with penalties by smelters)
- metal production can be applied on site.

Nevertheless this technology presents the following drawbacks and weak points:

- necessity of large surface for implementation
- relatively slow and limited recovery of some metals.

The second biotechnology that can be applied for metal recovery is known as the stirred tank technology. A bioreactor is continuously fed with a finely milled mineral suspension. The pulp is agitated and aerated in the tank where the main key operating parameters can be monitored and controlled. There are currently more than 14 plants in operation at industrial or demonstration scale for gold, Co, Cu and Ni (Rawlings et al, 2003). The main designers & operators are: BHP Billiton, Bactech, Mintek, BRGM, Gold Fields, and Codelco.

The principal reasons for selecting the stirred tank technology over other type of alternatives can be summarised as follows:

- attractive capital and operating costs and short construction and starting-up period
- relatively cheap environmental requirements (stable wastes)
- robust and simple process
- production on site of pure metal directly saleable on market
- on the other hand, this technology presents some weak points:
- limitation of the recovery on certain type of minerals
- energy requirements for mixing and oxygen.

Some extended and complete reviews were recently published concerning the role of biotechnology in the mining industry in general, and more specifically in the copper industry (Clark et al., 1995 ; Crundwell, 2005 ; Watlings 2006).

From a general point of view and in the case of copper extraction technologies, the choice of the best technology is driven by both the metal grade in the ore and the total amount of resource. Nevertheless, the main conclusion of the macro economic study (Pelon, 2006) is that the feasibility of a process on a given resource is strongly dependent on many site/resource specific factors.

Pyrometallurgy remains the main technology for metal recovery in general and especially for copper extraction. Nevertheless, there are more and more potential niches for application of biohydrometallurgy. Nowadays, biohydrometallurgy is taking an important place in the mining industry of non-ferrous metals either in competition or in complement of classical technologies. It is definitely offering to the mining

operators an alternative development option with inherently attractive economics. But although these technologies are used commercially in many countries, there have been relatively very limited developments in Europe. It remains to be clearly demonstrated that these technologies can:

- be used on a wider range of mineral resources, including metal-bearing wastes of the mining industries
- be economically viable and technically robust, with reasonable energy and water consumption and acceptable waste production
- help to reduce the environmental impact of the mining industry
- benefit from an expansion of the knowledge base, especially of microbiological aspects.

MAJOR ACHIEVEMENTS (PROCESS OPTIONS AND ACADEMIC R&D)

In terms of process development, the work carried out in the frame of Bioshale is focused on two case studies, involving two contrasting “black shale” deposits located in Poland (Lubin Mine) and in Finland (Talvivaara deposit). The most likely successful process options operations were developed early on in the project. In both cases, the work on process options assessment took into account the current situation on the target sites.

In the case of Lubin, there is an existing concentrator plant combined with a smelter that extracts mainly copper and silver. A copper concentrate is produced there, along with an “enriched shale fraction” (or “middlings”) which causes trouble in the flotation circuits. A second mine (Polkowice) located close to Lubin produces a similar concentrate, but which is more enriched in PGEs. Lubin ore contains disseminated sulphidic particles, closely associated with organic matter.

The most valuable metal in the Talvivaara deposit is Ni, while Co, Zn and Cu are also present in significant quantities. Currently a large-scale industrial project evaluating heap leaching technology to recover metals from the Talvivaara ore is under evaluation. The Talvivaara black shale is a metamorphosed black shale that contains mainly graphite.

LUBIN ORE/CONCENTRATE PROCESS OPTIONS

Many bioshale process options were considered by the consortium during the first two years of the project (Table 2). Cu and Ag recovery would be expected downstream of all of the Polish material options, except primary bioheap leaching of the ore which would not facilitate Ag extraction.

Bioleaching tests showed that the Lubin black shale middlings and concentrate fractions were amenable to bioleaching, with extraction of up to 98% of the copper (options 2 and 3). A variety of microorganisms from different phylogenetic groups

were used successfully at widely different temperatures, ranging from 30°C with mesophiles and 45°C with moderate thermophiles to 78°C with thermophiles. This leaching at low pH by acidophilic chemolithotrophic bacteria involved significant consumption of sulfuric acid.

Table 2. Bioshale process options (Polish case study)

Bioshale Process Options	General Description
Option 1: Bioheap leaching of Lubin run-of-mine ore	Classical bioheap leaching of Cu using agglomerated Lubin ore
Option 2: Leaching of Lubin middlings after pre-treatment	Bioleaching (or atmospheric chemical leaching) using middlings after acid pre-treatment for carbonate decomposition
Option 3: Bioleaching of Lubin concentrate (after pre-treatment)	Bioleaching using Lubin concentrate (after acid pre-treatment for carbonate decomposition)
Option 4: Selective flotation of Lubin run-of-mine ore + (Bio)leaching	Selective flotation of Lubin RoM to produce an enriched shale concentrate further treated using acid leaching for carbonate decomposition and bioleaching
Option 5 - Selective flotation of Lubin middlings + bioleaching	As option 4, but with middlings in place of ore
Option 6 - Selective mining + bioleaching	Selective mining of the deposit to separate the shale fraction. The enriched shale fraction would be treated using bioleaching

Although a range of heterotrophic microorganisms as well as some basophilic chemolithotrophs were able to leach copper from black shales, the results were far inferior to those obtained with chemolithotrophic acidophiles. Biodegradation of the organic matrix of black shales (Lubin ores and concentrates) was more difficult to achieve. No evidence of biodegradation was found with acidophilic heterotrophic bacteria. Experiments with neutrophilic microorganisms were more successful, but their positive impact on metal recovery efficiency remains to be demonstrated and quantified at larger scale.

Bioleaching using the Lubin concentrate after acid pre-treatment for carbonate decomposition was selected during the initial bioprocess selection (Fig. 2). This option is not yet of direct interest in the context of the current industrial process with the Lubin concentrator. It could become an option in the case of 'capacity shortage' in the smelter, or production of a 'dirty' concentrate (e.g. presence of arsenic).

Following successful batch culture tests with the pre-treated materials, processing in continuous conditions is necessary to determine the specifications for the application of the stirred tank technology to a sulphide concentrate from black shale ores. The work carried out on the downstream processing is also a technical challenge and more specifically the recovery of silver from the bioleached residues. Preliminary

results showed that more than 90% of the copper and more than 85% of the silver respectively can be extracted using the continuous stirred tank technology. Better performances are expected to be obtained following optimisation steps.

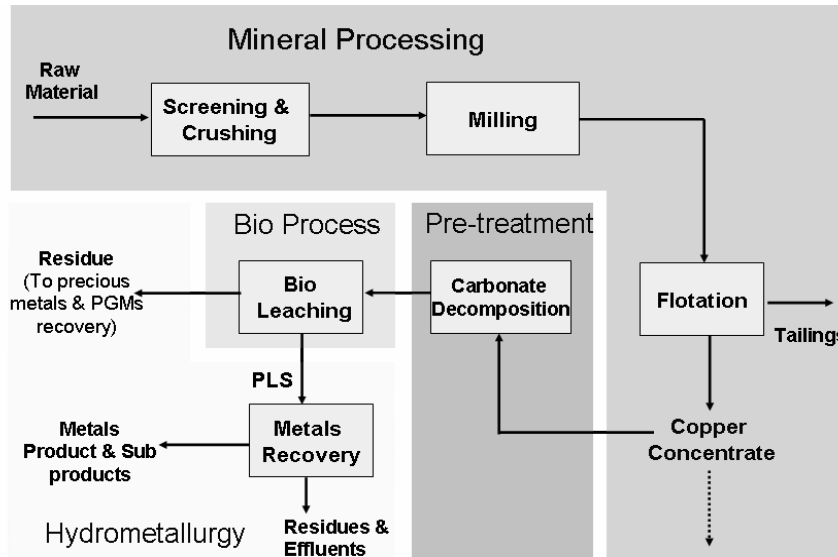


Fig. 2. Bioshale process option N°3 - Bioleaching of Lubin concentrate (after pre-treatment) (From TR - F. Sánchez and J. Palma ; From BRGM - D. Morin and P. d'Hugues)

Several process options concerning the Lubin middlings (Fig. 3) were considered.

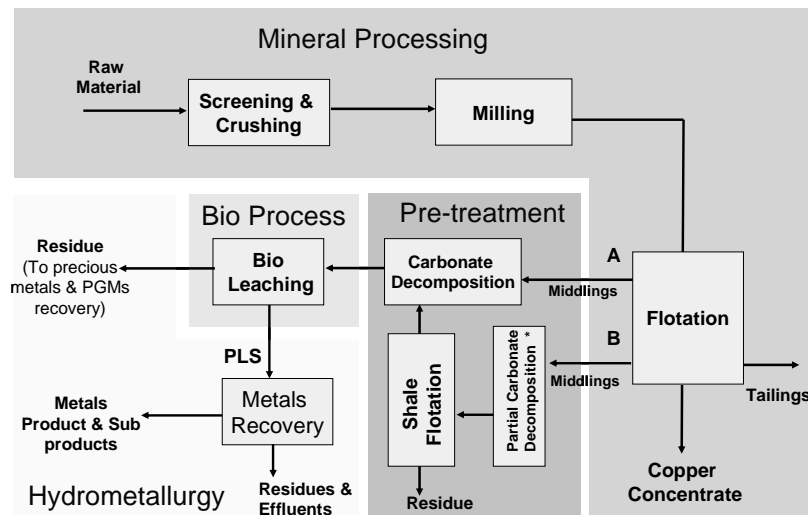


Fig. 3. Bioshale process option N°2 and N°5 - Bioleaching of Lubin middlings (From TR - F. Sánchez and J. Palma and PWR - A. Luszczkiewicz and T. Chmielewski)

This material has very similar properties to the shale ore. It was estimated that with the operation of the Lubin concentrator, the tailings of the first cleaning flotation represent 20-30% of the mass of solids in the whole flotation system, with copper recovery about 20-25%. Although it was demonstrated at laboratory scale that the material is relatively easy to bioleach, and its use could reduce the material flow in, and improve the total efficiency of, the flotation circuit, a direct (bio)leaching of the middlings does not look like economically viable because of the low copper grade. Agglomeration of this very fine material would be necessary prior to an alternative, bioheap treatment, and, although technically difficult, could be considered further.

Selective shale flotation (including bioflotation) of the Lubin Middlings (option 5) was tested. The flotation experiments proved that upgrading middlings is very difficult. It is necessary to produce enough high copper grade concentrate for further bioleaching before this option can be considered further. In conclusion, the technical and economical viability of any process on Lubin middlings remains very uncertain. The real consequences of bleeding the middlings stream are still not perfectly known and difficult to evaluate.

Two stage bioleaching of Lubin middlings (option 7) was also considered (Fig. 4) in case it was demonstrated that shale organic matter degradation was necessary to recover rare and noble metals. Biodegradation of organic matter, extracted from the shale, and synthetic metallo-organic complexes (metallo-porphyrins), were examined at neutral pH. So far, any added value of the neutral leaching stage was not demonstrated. The preliminary results indicate that this option is not applicable in the context of Lubin mine, but might be of interest with black shale samples enriched with rare and noble metals encapsulated in the organic matter.

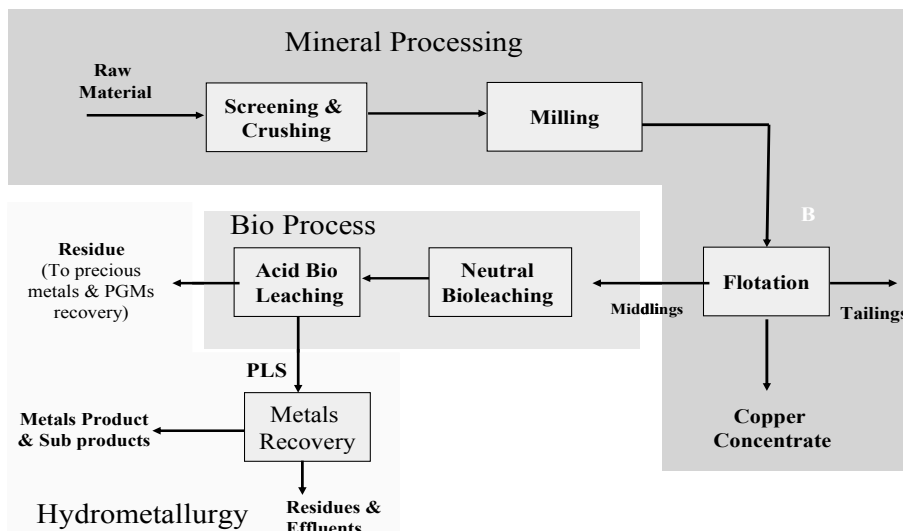


Fig. 4. Bioshale process option N°7 – Two stages bioleaching of Lubin middlings (From PWR and UO - Z. Sadowski and T. Farbiszewska)

ACADEMIC ASPECTS

In addition to the development of bioprocess options, some more academic scientific research has been carried out during the first two years of the Bioshale project.

1. Production of new scientific data on noble metals occurrence (PGE,...) in black shales.
2. Research into the identification of noble metal carriers in metal rich shales in order to explain the mechanism of the origin of noble metals in various black shales worldwide.
3. Participation in the development of bioleaching technologies for copper recovery that can be applied to multi-element (metals) concentrates and black shale ores.
4. Optimisation of silver recovery from residues after bioleaching. Demonstration of the ability to bioleach metals from black shale ores that contain organic matter.
5. Study of phenomena governing bacterial adhesion, role of cell surface properties in adhesion and bioflotation processes.
6. Bioprospecting at all three sites for (novel) bioleaching microorganisms.
7. Study of the microbial ecology of the TVK heap using molecular biology tools. Modelling and simulation of heat transfer using data from both pilot operations (GTK and TVK).

The reports that were produced by the Bioshale consortium since the beginning of the project are presented in Table 3. All these reports are confidential, but abstracts are available on the Bioshale web site (<http://bioshale.brgm.fr>) and the main results will be freely disseminated during and after the final year of the project.

CONCLUSIONS

Between 2003, the preparation phase of the project, and the beginning of 2007, the project's final year, some changes occurred and some adjustments were made to the original programme. The beginning of the project coincided with a spectacular rise in worldwide commodity prices. Non-ferrous metals all witnessed a strong price increase over 2005 and early 2006, that was sustained over 2006 (Lips, 2006). This phenomenon was notably observed on copper, nickel and zinc, and the Talvivaara mine project became a likely commercial reality. Chemical analysis of samples from the Lubin area did not show any high concentration of rare/strategic metals or PGE in the organic matter. The technical issues related to the accumulation of shale fractions (middlings) in the flotation circuit of the mineral processing step at Lubin was clearly identified as an important target for the project. The consequence of all these issues on the Bioshale project was that the recovery of base metals (Cu, Ni, Zn) from black shale ores became the main priority over the challenge of the recovery of valuable minor metals (PGE, V, Re, etc.) potentially trapped in organic matter. The (bio)processing R&D actions on Polish ores and concentrates from Lubin Area have

been focused mainly on copper and silver recovery. The various process options presented in this paper have been investigated or are still under investigation. The most promising ones will be assessed against technical, economic and environmental criteria. The results of these pre-feasibility studies will be presented at the end of the project.

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Projekt BIOSHALE, obejmujący 13 partnerów z Europy, jest sponsorowany przez Unię Europejską w ramach programu FP6. Głównym przedmiotem badań w tym projekcie, który rozpoczął się w październiku 2004r., jest znalezienie i opracowanie innowacyjnego procesu biotechnologicznego, który umożliwi eksploatację w sposób ekologiczny rud łupkowych bogatych w metale. Badaniem poddane zostały trzy istniejące złoża. Są nimi: (i) złoże Talvivaara w Finlandii, które w momencie rozpoczęcia projektu nie było eksploatowane, (ii) złoże Lubińskie w Polsce, które jest obecnie eksploatowane, (iii) trzecim miejscem były okolice miejscowości Mansfeld w Niemczech, gdzie została zakończona eksploatacja i pozostały hałdy odpadów. Rudy łupkowe zawierają metale takie jak: miedź, nikiel, metale szlachetne (głównie srebro) oraz metale z grupy platynowców (PGM), a także duże ilości substancji organicznej, która uniemożliwia odzysk tych metali w sposób konwencjonalny.

Głównymi aspektami pracy w projekcie są:

1. opis zasobów geologicznych i wydzielenie składników (rud) bogatych w metale,
2. wybór konsorcjum bakteryjnego dla prowadzenia procesu bioługowania,
3. ocena procesu bakteryjnego ługowania łącznie z procesem hydrometalurgicznym,
4. opracowanie założeń techniczno-ekonomicznych nowego procesu odzysku metali,
5. ocena ryzyka zagrożenia środowiska naturalnego przez wprowadzenie procesu bazującego na biotechnologii w porównaniu do istniejących procesów.

W pracy został dokonany przegląd najważniejszych wyników ze szczególnym wyróżnieniem technologii bioługowania w celu odzysku metali. Technologie tę można będzie zastosować do przerobu wieloskładnikowych koncentratów i rud łupkowych w Polsce.