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Biohydrometallurgy applied to exploitation of black shale resources: Overview of Bioshale FP6 European project

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Abstract: Bioshale project, co-funded by the European Commission (FP6 programme), started in October 2004 and finished in October 2007. The main objective of this project was to define innovative biotechnological processes for "eco-efficient" exploitation of black shale ores. The black shale ores contain base, precious and high-tech metals but also high contents of organic matter that handicap metal recovery by conventional techniques. Three world class black shale deposits were chosen as targets of the R&D actions. These include one deposit that existed under natural conditions (Talvivaara, Finland), one currently in process (Lubin, Poland) and one after mining (Mansfeld, Germany). The main technical aspects of the work plan can be summarized as follows: evaluation of the geological resources and selection of metal-bearing components; selection of biological consortia to be tested for metal recovery; assessment of bioprocessing routes, including hydrometallurgical processing for metals recovery; techno-economic evaluation of new processes including social and environmental impacts. An overview of the main results obtained by the 13 European partners (from 8 countries) involved in this completed research programme is given in this work.

Key words: bioleaching; biotechnology; mineral processing; black shales

1 Introduction

Biohydrometallurgy has often been promoted as a more environmentally friendly approach to processing mineral ores and concentrates than conventional practice, such as pyrometallurgy. The European Commission supported two projects involving mineral biotechnology in the Sixth Framework Program for Research and Development: BioMinE[1] and Bioshale[2]. The Bioshale project examined the potential of bioprocessing "black shale—Kupferschiefer" ores, to recover both base and precious metals. The potential applications of biohydrometallurgical technologies for the recovery of metals from sulfide ores and concentrates are well established[3], but it is not known whether or not organic-rich black shale ores present peculiar problems (or indeed advantages) that could severely impact bioprocessing using established biological systems and engineering protocols.

All aspects concerning Bioshale project programme were already published[2]. This paper summarises the main information on the project and describes the main results that were obtained during the project, with particular emphasis on biotechnological aspects.

2 Project description

Bioshale was a project co-funded by the European Commission (FP6 programme) that started in October 2004. The main objective of Bioshale was to define innovative biotechnological processes for "eco-efficient" exploitation of black shale ores.

Such ores contain base, precious and "high-tech" metals (Cu, Ni, Zn, Ag, Co, Pt, Pd, V, etc.) but also high contents of organic matter that handicap metal recovery by conventional techniques. Three extensive deposits were selected for R&D actions. These are: 1) a site that, at the outset of the project, had not been exploited (in Talvivaara, Finland); 2) a deposit that is currently being actively mined (in Lubin, Poland), and 3) a third site where the ore had been actively mined in the past, but is no longer exploited (in Mansfeld, Germany).

The social and economic benefits of the project included the continuation of mining activities in Europe (Lubin/Polkowice) and to help exploit new resources with considerable reserves (Talvivaara). The Mansfeld site was illustrative of and supports the evaluation of the

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environmental impact of black shale ore exploitation.

The main tasks of Bioshale project can be summarised as follows:

1) Evaluation of the geological resources (geological modelling);

2) Selection of metal-bearing components and biological consortia to be tested;

3) Assessment of bioprocessing methods and determination of complementary hydrometallurgical processing routes for metals recovery;

4) Use of new analytical tools based on molecular biology for the characterisation and monitoring of bacterial communities;

5) Risk assessment relative to management of waste material from the new processing routes; and

6) Techno-economic evaluation of new processes from mining to metal recovery including social and environmental impacts.

From an administrative point of view, the Bioshale project was a Specific Targeted Research Project in the FP6 programme (contract-NMP2-CT-2004 505 710). The project duration was 3 years, and the total budget was 3.4 M€ (EC contribution 2.3 M€). A consortium with partners from different fields was established (Table 1).

The project was also dependent on the kind collaboration of the owners of the ore deposits: KGHM Polska Miedź S.A. (Poland) for the Lubin deposit and concentrator and TVK, Talvivaara Mining Company Ltd (Finland) for the Talvivaara deposit. The Talvivaara deposit was bought by TVK, after the project was planned but before it started.

3 Development of bioprocess options

From a general point of view, and in the case of copper extraction technologies, the choice of the best technology is usually driven by both metal grade in the ore and total amount of resource. It was demonstrated that the feasibility of a process on a given resource was also dependent on many site/resource-specific factors. Pyrometallurgy remains the main technology for metal recovery in general and especially for copper extraction.

Table 1 Bioshale consortium description

Participant name	Country	Role
Bureau de Recherches Géologiques et Minières	France	Project coordination/WP5 leader—R&D activities in microbiology, biotechnology, geology, mineralogy and 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 and mineral processing
University of Warsaw-Faculty of Biology—CEMERA	Poland	Topic leader (environmental impacts)—R&D activities in microbiology, biotechnology and environmental impacts
Geological Survey of Finland	Finland	WP6 leader—R&D activities in mineral processing, biotechnology, mineralogy, environmental impacts and socio-economy—sample provider
Helsinki University of Technology	Finland	R&D activities in geology, mineralogy, electrochemistry and environmental impacts
Tecnicas Réunidas	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 and 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 and mineralogy

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. Biohydrometallurgy definitely offers an alternative development option with attractive economics to the mining operators.

In term of process development, the work carried out in the frame of Bioshale was focused on two case studies, two types of black shales materials situated in Poland (Lubin/Polkowice Mine) and in Finland (Talvivaara deposit).

The most reasonable process options operations were described in the first 6 months of the project. These preliminary process options were studied by Bioshale consortium with the objective to develop new bio-hydrometallurgical routes for the recovery of valuable metals from black shale ores and/or concentrates. From the first results obtained in the different laboratories, some new options were also proposed by Bioshale consortium.

In both cases, the work on process options assessment took into account of the current situation on the target sites in Poland and in Finland.

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 it 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. At the beginning of Bioshale project, a large-scale industrial project evaluating heap leaching technology to recover metals from the Talvivaara ore was under evaluation. The Talvivaara black shale is a metamorphosed black shale (black schist) that contains mainly graphite.

Combining all participant contributions, a detailed analysis of all process options including their strengths and weaknesses was carried out and presented in Bioshale mid-term report. The main conclusions concerning the process alternatives can be summarized for the principle "samples'' of Bioshale project (Lubin and Talvivaara).

3.1 Lubin process options

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. A variety of microorganisms from different phylogenetic groups were used successfully at widely different temperatures, ranging from 30 ℃ to 78 ℃ [4−7]. 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 have been much successful; and their positive impact on metal recovery efficiency remains to be quantified at larger scale.

Amongst the various process options tested, two were examined in more details:

1) Continuous bioleaching of Lubin copper concentrate using stirred tank technology; and

2) Bioleaching (or atmospheric leaching) of middlings after acid pre-treatment to destroy carbonate minerals, or after selective flotation.

Following successful batch culture tests with the pre-treated (non oxidative acid leaching) materials, processing in continuous conditions was realised to determine the specifications for the application of the stirred tank technology to the Lubin copper concentrate from black shale ores (Fig.1). The work carried out on the downstream processing was also a technical challenge, specifically the recovery of silver from the bioleached residues.

The best copper recovery obtained in the continuous operation was 92%, and a hot brine leaching of the bioleach residue (PLINT process[8]) allowed to recover 92% of the silver. A preliminary techno-economic evaluation of Lubin concentrate bioprocessing including bioleaching, copper and silver recoveries demonstrated the potential economic feasibility. Recovery of silver plays an important role in the economy of the process. A comparative analysis of the new bioprocessing route with other processing technologies was performed. The comparison showed that "Bioshale process" costs were comparable with the existing technologies, with a lower investment cost in comparison with the smelting technology[4].

Several process options concerning the Lubin middlings were considered. This material has very similar properties to the shale ore. It was demonstrated at laboratory scale that the material was relatively easy to bioleach. Its use could reduce the material flow in the flotation circuit, and improve the total efficiency of the latter. Nevertheless, a direct (bio)leaching of the middlings did not appear to be economically viable

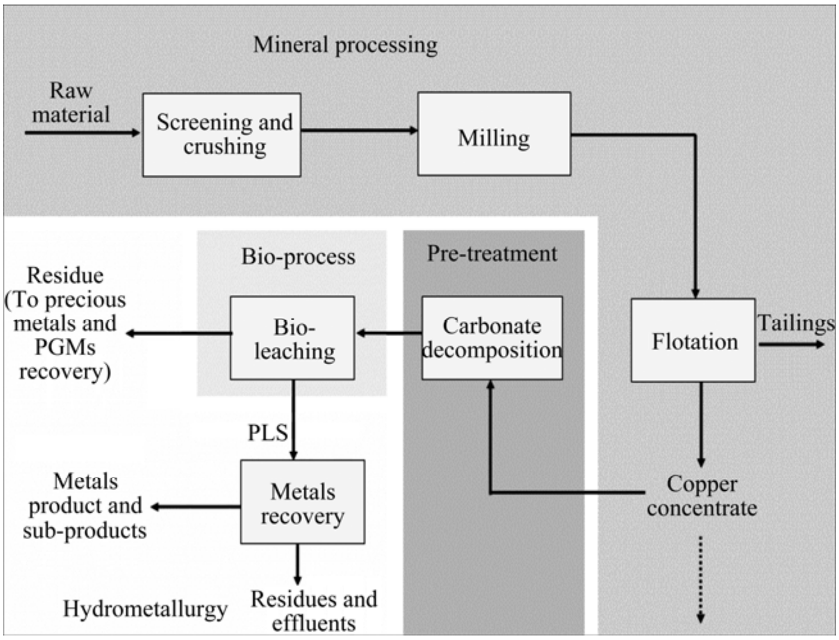

Fig.1 Bioshale process options on Lubin samples: bioleaching of copper concentrate

because of the low copper grade.

Selective shale flotation (including bioflotation) of the Lubin middlings was tested. The flotation experiments proved that upgrading the middlings was very difficult[9].

Atmospheric leaching of Lubin shale middlings with oxygenated sulphuric acid and with addition of Fe(III), performed at temperature up to 90 ℃, clearly showed that the process can be effectively applied, due to the favourable mineralogical composition[10].

Two-stages bioleaching of Lubin middlings (neutrophilic + acidophilic bioleaching) was also considered in case that it would be 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), was examined at neutral pH[11].

In conclusion, direct bioleaching of the concentrate is technically and potentially economically feasible. The option of bioleaching the middlings in perfectly agitated tanks (or the atmospheric leaching) looked economically unattractive, while the consequences of bleeding the middlings stream on the material balance of the entire circuit are still not established and difficult to evaluate.

3.2 Talvivaara process options

The Talvivaara deposit belongs to the Talvivaara Mining Company Ltd. The grade of the Zn-Ni concentrate obtained from Talvivaara ore remains too low to make continuous stirred bioreactor technology viable. From a technical point of view, two pilot plant experiments, using heap bioleaching technology, were carried out simultaneously on Talvivaara ore: one of them by the Geological Survey of Finland (GTK) within the Bioshale project and the other at the deposit site by the Talvivaara Mining Company Ltd[12].

In Bioshale project, several R&D actions were undertaken both on the GTK tower (simulation of heap leaching technology) and on TVK bioheap leaching demonstration operation (on site). These actions included microbial monitoring by molecular biology[13]; complementary bioleaching tests at lab-scale (designed consortia; high temperature column leaching, etc)[14]; and modelling of heat transfer in the bioheap. The work was coordinated in collaboration with TVK (Fig.2).

The GTK pilot column for heap bioleaching tests was inoculated with a mixed culture of acidophiles enriched from waters near the Talvivaara ore body. In March 2005, the pilot column tests started at outdoor temperatures of −10 ℃ and reached +25 ℃ warm effluents containing Fe, Mn, Zn and Ni within a week, providing a strong indication of the applicability of the process in sub-arctic environmental conditions.

The TVK demonstration heap indicated that high temperatures (up to at least 80 ℃) were an inherent part of the process operation. It provided direct relevance to the investigation of microbial activity in metal extraction at high temperature. Laboratory leaching columns were used to simulate the heap leaching process. The role of the microorganisms in extraction of various metals from the ore (nickel, zinc, cobalt, and copper) was established and the advantages of a microbial process were clearly demonstrated.

Fig.2 Development of heap bioleaching operation in Finland by TVK company on Talvivaara deposit

The positive effect of decreasing ore particle size on leaching efficiency was demonstrated at 37 ℃ using a mixed population of acidophiles, including mesophilic and moderately thermophilic acidophiles. Manganese and nickel were leached effectively in columns. The composition of the microbial population radically changed over the 40 weeks incubation period. Indigenous (Gram-positive) acidophiles were frequently detected in mineral leachates and were particularly important in the early stages of mineral dissolution.

The microbial monitoring of the pilot bioleaching tests, on-site in Talvivaara and at GTK in Outokumpu, was implemented. The microbial populations in each operation were studied by cultivation (e.g. enumeration and isolation of acidophiles on solid media) and by biomolecular analysis.

A wide range of acidophiles have been isolated from samples of the heap solutions and solids, and include many acidophiles known to be important in bioleaching. These include both mesophilic and moderately thermophilic acidophiles, with the former type proving to be more prevalent.

In June 2007, TVK decided to invest 452 MEUR for the period from 2007 to 2010 for the development of the mine. The Talvivaara deposit has about 340 Mt of resources. The anticipated production is equivalent to 2.3% of the world Ni-production, and thus will increase Europe's Ni production by 100%.

4 Academic research actions—main outputs

In addition to the development of bioprocess options, some more academic scientific research was carried out during 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) Demonstration of the ability to bioleach metals from black shale ores that contain organic matter.

5) Optimisation of silver recovery from residues after bioleaching.

6) Study of phenomena governing bacterial adhesion, role of cell surface properties in adhesion and bioflotation processes.

7) Bioprospecting at all three sites for novel bioleaching microorganisms, especially those suitable for use in the various bioprocessing options considered in the Bioshale project.

8) Extension of the known habitats of mineral oxidising acidophiles, as well as general characterisation of microbial populations associated with black shale ores.

9) Study of the microbial ecology of the TVK heap using molecular biology tools.

10) Modelling and simulation of heat transfer using data from both pilot operations (GTK and TVK).

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