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Bioleaching of Kupferschiefer blackshale – A review including perspectives of the Ecometals project

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ABSTRACT

In Europe, most of the primary copper resources that possess a high or moderate amount of metals, have a reasonable accessibility and are easy to process are exhausted. In this context, low grade and complex ores as well as old waste deposits related to past mining activities are receiving increasing attention. For an economic exploitation of such ores and resources, with quite different mineral matrix, new and efficient methods need to be developed. Bioleaching is a reliable and promising option.

Among the different kinds of copper mineralisation that can be found in Europe, sulphidic Kupferschiefer deposits have been explored and exploited for years in Germany and Poland. They are Europe's largest copper reserve with more than 60 million tons of Cu, and contain additional associated metals such as Ag, Pb, Zn and possibly other high-value metals. Kupferschiefer deposits are currently under exploitation in Poland, but process operations are more and more penalised by the significant amounts of organic matter and arsenic present in this type of ores. Therefore bioleaching is more and more considered as a credible alternative to the pyrometallurgical technology which may no longer be feasible in future given the concentrate chemistry.

In this context, this paper provides an overview of the previous work on the geology, mineralogy, and (bio)processing of the Kupferschiefer. It will also present new opportunities and challenges related to the development of innovative methods for metal recovery by means of biotechnology.

Generally, bioleaching of Kupferschiefer is influenced by the mineralogical nature of sulphides and organic matter contained in the ores. For example, recalcitrance of chalcopyrite during leaching is a major limitation of biohydrometallurgy applied to copper ores in general and blackshales in particular. Organic matter, moreover, causes also flotation problems. However, the organic materials especially the metall-organic compounds containing platinum group (PGE) or rare earth elements (REE) may make processing of Kupferschiefer economically interesting.

The first works dealing with Kupferschiefer bioleaching in Europe date back more than three decades, and were pursued again beginning of the 21st century in the European Bioshale project. This project demonstrated the overall efficiency of continuous stirred tank reactors (CSTR) bioleaching of a blackshale concentrate with an extraction rate above 90%. Nevertheless, two possible improvement paths were identified: reducing the tank size or improving chalcopyrite dissolution affecting the operation efficiency. These challenges were then further addressed in ProMine project opening new perspectives for bioleaching of Kupferschiefer ores which will be dealt with in the French–German project Ecometals.

1. Introduction

The increasing worldwide urbanisation and industrialisation has led to an increased demand of industrial metals such as copper.

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Copper is widely used not only in electronic devices, but also for water lines, electrical circuits and transport systems. With a production of more than 5 million tons per year, Chile is the most important copper ore producer (USGS, 2014). In Europe, several copper mines are operating in Russia, Poland, Portugal, and Sweden. Among the different kinds of copper mineralisation in Europe, sulphidic Kupferschiefer deposits have been explored and exploited for years in Germany and Poland. Kupferschiefer is a calciferous, carbon rich marly clay with finely dispersed sulphidic copper minerals, mainly chalcocite, bornite, and chalcopyrite. Besides copper, this type of ore can also contain up to 20 other valuable metallic and metalloid elements that are of increasing strategic value in Europe (EC, 2014). Furthermore, Kupferschiefer shaly facies are known to contain significant amounts of kerogen and also arsenic, both penalizing current pyrometallurgical processes.

Kupferschiefer deposits are currently exploited in Poland in the districts of Lubin, Polkowice and Rudna by KGHM company. Germany also possesses significant copper ore deposits. The region of Spremberg was recently explored by the enterprise KSL GmbH and the region of Weißwasser, Lusatia is currently explored by the enterprise KGHM Kupfer AG, Weißwasser. In the Mansfelder Land, Kupferschiefer was mined until 1990. Many waste dumps remind of the mining history of this region. These wastes contain copper that could not be recovered by the former processing technology as well as associated metals that were not exploited in the past, and thus can be considered as potential low grade resources.

In Poland, Kupferschiefer ore treatment means a first grinding step followed by flotation. Unrefined metals are then produced from the concentrate through pyrometallurgical smelting. In the last 5–10 years, exploited ore characteristics changed. An increase of organic carbon and arsenic contents as well as a decrease of the copper content in the ore has been observed. This change in the ores' specific properties worsens concentrate quality and has raised different kinds of issues in the smelting operations. Unsuitable levels of temperature, mainly due to improper organic carbon content, have been observed during the copper matte production, leading to smelter damage. Arsenic emission with the fumes produced during smelting process is also regarded as an important environmental issue all over the world and lead to important financial penalties for the smelter operators.

Considering all these aspects, exploitation of Kupferschiefer deposits, either for current operations in Poland or for potential new operations in Germany will require developing alternative and complementary routes to conventional smelting processing. Besides environmental concerns, economic aspects have also to be taken into account: due to high capital and operational costs (e.g. energy costs) smelting is usually dedicated to the treatment of high grade copper concentrate. In the case of Kupferschiefer ores, the flotation index is expected to be poor in any cases with respect to the high carbon content, which should lead to low grade copper concentrate. In this context, hydrometallurgy and more specifically bioleaching is considered as an ecologically acceptable and yet economic alternative. Progress in the construction of leaching plants, the construction and management of heap bioleaching operations as well as in the process design resulted in a worldwide spreading of the technology. As an example, it is estimated that about 15% of the world's copper production is currently facilitated by microorganisms (Schippers et al., 2014). In addition, bioleaching appears more and more industrially proven as a portfolio of flexible techniques to provide a way of recovering base metals in low grade ores and mining wastes, particularly when they contain deleterious elements that result in heavy penalties in pyrometallurgical treatments. Several research projects dedicated to bioleaching developments for Kupferschiefer ore processing have already been carried out. The efficiency and economic interest of this technology for black shale treatment have been demonstrated (Bosecker, 1997; Spolaore et al., 2009; Guezennec et al., 2014). The purpose of this article is (i) to summarise information and scientific data from the literature dedicated to bioleaching of copper black-shale ores and (ii) to give an overview of promising developments for the implementation of bioleaching operations dedicated to Kupferschiefer ore treatment. A special emphasis will be put on the recently started German–French R&D project Ecometals (for further information consult the project's website at http://www.ecometals.org).

2. Kupferschiefer mineralogy and organic matter description

2.1. Main characteristics

The German and Polish copper mining district of the Kupferschiefer ores (Fig. 1) contains Europe's largest known copper reserve and represents also globally one of the largest sediment-hosted copper systems. Pre-mining reserves, i.e. mined and proven, comprised more than 3 billion tons of ore with more than 60 million tons of contained copper, plus several other metals (Ag, Pb, Zn, and minor amounts of Co, REE, Ni, Mo, Au, PGE, etc.).

Kupferschiefer ore has been mined at least since 1190 AD in Germany, but pre-historic mining of supergene, i.e. surface-oxidised, malachite and azurite ores is highly likely. Several large active mines are operating in Lubin, Rudna and Polkowice-Sieroszowice, SW-Poland by KGHM, Europe's largest primary copper producer. A comprehensive review of the exploration and mining history, as well as a detailed summary of the geology, mineralogy, and past and present metallogenetic concepts has been published recently by Borg et al. (2012), from which the following condensed summary has been extracted.

The ores occur in the Permian black C_{org}-rich shale of the Kupferschiefer *sensu stricto* (s.s.), in footwall sandstones, conglomerates of the Rotliegend, and in the hangingwall Zechstein limestones (Fig. 2). The mineralised zone is – at a shallow angle – transgressive to stratigraphy and comprises a more narrow zone in the Mansfeld–Sangerhausen district (generally < 1 m), a thicker zone in the Spremberg-Weißwasser district (10–15 m), both Germany, but is up to 35 m thick in the Polish mines. Sandstone is the main host rock to the ore in Rudna and Lubin mines (84% and 79%, respectively) and 60% of the ore is limestone-hosted in Polkowice mine. Similarly, in the Spremberg exploration district only 46 % of the ore is black shale-hosted, whereas 31% is sandstone-hosted and 23% is limestone-hosted.

The regional and local distribution of the mining districts and ore bodies is structurally controlled by NW–SE and NNE–SSW trending faults and shear zones and particularly by intersections of these fracture systems. The black shale horizon (T_1) hosts synsedimentary to very early diagenetic pyrite but no substantial amounts of Cu-sulphides. Ore textural evidence shows that the Cu-, Pb-, Zn-, Co-, Ni-sulphides are of late origin since they have replaced early (framboidal) pyrite and pyrite cubes, carbonate cements and carbonate layers, fossil shells, feldspar clasts. The mineralisation occurs also in cross-cutting and bedding-parallel veins, veinlets and as a matrix to tectonic breccias. All of these types of mineralisation have been referred to by the dump-term "Kupferschiefer", which is not really helpful for metallogenetic interpretations. Absolute paleomagnetic age dating has revealed two mineralisation ages at 149 Ma and 53 Ma (Symons et al., 2010), which relate to major tectono-magmatic events (see Borg et al., 2012 for details).