Minerals Engineering 119 (2018) 23–30

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

Mineralogical distribution of base metal sulfides in processing products of black shale-hosted Kupferschiefer-type ore

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ARTICLE INFO

Keywords:
Black shale
Particle analysis
Bioleaching
Chalcopyrite resistance
Flotation pre-treatment
Dextrin

ABSTRACT

The extraction of copper from black shales associated with fine-grained and complex base metal ore mineralization traditionally using pyrometallurgy becomes increasingly uneconomic, because one of the most significant cost factors is the high energy consumption. Thus, energy-saving alternative mineral processing methods are to be considered to improve the metal recovery route economically and environmentally. In this study, a milled, organic carbon-rich black shale ore from the Sangerhausen mining district in central Germany has been pre-treated by ethanol prior to the froth flotation tests to gain a copper concentrate marked by an increased copper content and more efficient copper recovery. The flotation product (15.3% Cu) was used for biohydrometallurgically batch tests to extract copper and associated trace metals. SEM-based automated particle analyses on the comminuted black shale ore, flotation product as well as tailings, bioleaching residues and abiotic leaching residues were used to trace the recovery performance particularly of copper sulfides. The black shale ore is characterized by high contents of bornite (2.8 wt%) and chalcopyrite (1.3 wt%) associated with a high grade of pyrite (5.8 wt%). Considerable enrichments were achieved in the flotation product for bornite (20.7 wt%) and chalcopyrite (10.3 wt%) as well as for galena and sphalerite, while pyrite was successfully depressed in the tailings. Compared to abiotic chemical leaching, the bioleaching test of the bornite- and chalcopyrite-rich copper concentrate was particular efficient in the recovery of bornite and chalcocite. However, chalcopyrite was leached insufficiently in both, abiotic and microbial leaching tests, and presents a common component in the residues.

1. Introduction

The recovery of copper from black shale-hosted ore was extensively practised pyrometallurgically in the former Kupferschiefer mining district of Central Germany and still represents the main copper winning technology of recently mined Polish Kupferschiefer-type ore. Volatile price developments on the metal markets and increasing production cost at currently decreasing copper content in the ore (Chmielewski, 2015) require more efficiency in the established process chain or the introduction of alternative energy- and resource efficient processing technologies. Such new processing options either aim at the adaption and improvement of existing process protocols, e.g., for froth flotation, or to the substitution of an uneconomic process unit, e.g. pyrometallurgy by (bio)-hydrometallurgy.

However, the flotability of black shale ore is a challenge due to its fine-grained intergrowth of valuable minerals and special carbonaceous and argillaceous composition. With regard to achieve improvements in the recovery of copper by froth flotation, numerous tests were carried out in recent decades. In 1932, Aletan (1932) investigated the flotation of black shale ore from Niedermarsberg and Mansfeld mines. He already described that the high content of organic compounds impairs a selective flotation of copper minerals. Babiński et al. (1978) and Kleiner (1987) reported a setback in the approach to increase the recovery of sulfides by flotation caused by the abundance of clay minerals and elevated organic carbon contents. Hamami (1980) paid close attention to eliminate or passivate the organic carbon in the flotation of black shale ore. For example, he tried to extract the bituminous components with solvents of the coal and oil shale extraction industry, but only reached low yields. Recent flotation tests of the UVR-FIA GmbH (Freiberg, Germany) with black shale ore promised a high copper recovery in combination with high copper content using a new pre-treatment method used for the flotation test investigated in this study.

As conventional copper extraction via smelting has been extremely energy-consuming, (bio)-hydrometallurgy in combination with

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https://doi.org/10.1016/j.mineng.2017.11.009
Received 30 April 2017; Received in revised form 10 November 2017; Accepted 27 November 2017

electrowinning represents a low-cost and environmental-friendly and energy-saving extractive method to win copper products. Studies on the processing of low-grade Kupferschiefer ore and dump material by bioleaching started in the 1970 s in laboratory and pilot scale percolator experiments to simulate heap bioleaching and has been relaunched recently (Kamradt et al., 2012). Further experimental work within the European project “Bioshale” (D’Hugues et al., 2007) lead from bench scale to pilot scale for bioleaching of a copper concentrate from KGHM Lubin mine in Poland. This was produced from an organic-rich ore by flotation. This carbonate-rich, multi-element (Cu, Ag) and polymineral concentrate contained chalcocite, bornite, chalcopyrite and covellite. Given the fine nature of the concentrate and its carbonate content, stirred tank bioleaching was applied instead of heap leaching. The best copper recovery obtained in the continuous operation was 92% within 6.6 days at 15% solids content in 60 L operating volume in three consecutive bioreactors, and hot brine leaching of the bioleaching residue (PLINT Process) permitted the recovery of 92% of the silver. Copper recovery seemed to be limited by incomplete chalcopyrite dissolution. Final copper recovery was higher in batch cultures (> 95%) than in continuous mode (Spolaore et al., 2009, 2011). Further experimental work on testing a higher solid load was done within the European project “Promine” (http://promine.gtk.fi/). The bioleaching performances at 25% solids were similar to those obtained in “Bioshale” with 15% solids at the same operating conditions. However, the incomplete dissolution of chalcopyrite was confirmed which remains a key issue for copper ore bioleaching improvement (Ahmadi et al., 2011; Schippers et al., 2014; Watling, 2006, 2015). Improvement required further investigations which are partly presented here in order to ensure an optimal control of the process for upscaling in the German-French project “Ecometals” (Kutschke et al., 2015).

2. Mineralogical characteristics of black-shale-hosted Kupferschiefer-type ore

The Permian black shale that represents the base unit of the Central European Zechstein basin is one of the world’s largest sediment-hosted copper deposit (Cox et al., 2007; Borg et al., 2012) and widely known as Kupferschiefer-type ore. Lithologically, the black shale is a fine laminated, organic matter-rich marl composed of varying proportions of quartz, carbonates, feldspars and clays. The grade of base metal sulfides can change from barren to highly enriched lateral sections within the black shale layer. Additionally, the base metal mineralization occurs lithologically layer-overlapping by transitional enrichment zones of sulfides in the footwall sandstone as well as in the hanging wall limestone sequence.

The black shale from the Sangerhausen mining district used as feed ore in this study is extremely rich in kerogen-type organic matter and marked by a total organic carbon content of 14.2%. It shows a typical layering and is dark anthracite due to the high portion of organic matter. Besides the layered rock fabric, the black shale ore is partly characterized by crosscutting barite and calcite veins containing sulfides as pyrite and chalcopyrite. The main part of the ore mineralization occurs as fine disseminated sulfide particles within the layered rock fabric, which often consists of intimately intergrowths of several sulfides or sulfides with gangue minerals (Fig. 1). The grain size of these particles is commonly between 40 and 60 µm. Another ore texture that can be observed in the black shale ore is indicated by bedding-parallel replacement fillings marked by more massive, up to several mm thick sulfides layers, in which the sulfides are partially intergrown more coarse-grained chiefly with carbonate minerals. The sulfide assemblage contains, in abundance order, mainly pyrite, bornite, chalcopyrite, chalcocite, galena and sphalerite. Accessories include tennantite, covellite and cobaltite.

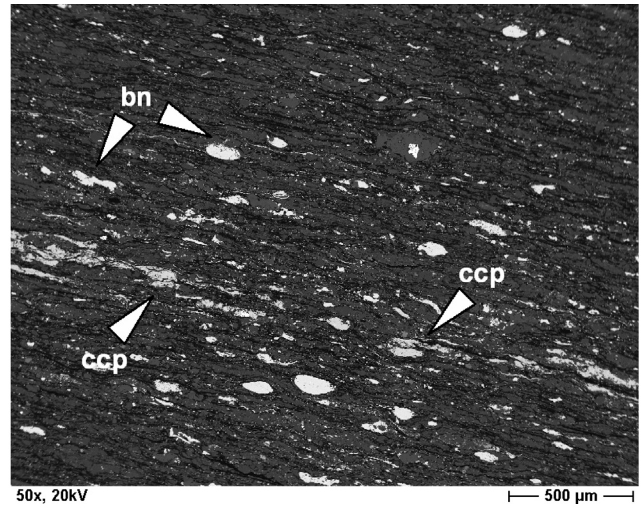

Fig. 1. Typical ore textures in Kupferschiefer-type black shales. The sulfide particles occur finely dispersed within the finely laminated rock matrix or form intricately intergrowths of several sulfides or gangue. Polished section, BSE-SEM-image, bn = bornite, ccp = chalcopyrite.

3. Materials and methods

3.1. Samples

A black shale bulk sample from central Germany of about 200 kg was provided by an underground drilling campaign in a ventilation tunnel of the “Roehrig” shaft, part of the Thomas Muentzer Mine in the former Sangerhausen mining district, Germany. 17 drill cores with 10-cm diameter and more than 1 m length of fresh, not oxidized sample material were extracted bedding-parallel and along the lower black shale base from a 15 m wide area of the tunnel. The whole sample material was crushed < 3.15 mm and a representative split of 100 kg was milled. The mean Cu-content of the ball mill product is 2.38% (95% CI: 2.34–2.41%) and was analysed on seven subsamples. The comminution was carried out with a primary jaw crusher, cone crushers and finally a screening ball mill, which delivered a comminution product with a final grain size of < 100 µm. The milled ore was used to perform flotation tests and generate a copper-rich concentrate. The copper concentrate in turn was utilized for bioleaching batch tests. Black shale ore, flotation product and tailings as well as residues from bioleaching and sterile control tests were investigated in this study.

3.2. Flotation tests

The flotation was carried out with a lab-scale DENVER flotation machine (1.2-liter-cell) with a solid content in the flotation feed of about 30%. The pH value 10 was adjusted with sodium hydroxide, as dispersing agent 150 g/t polyacrylate was added. Dextrin (1500 g/t) was applied to diminish the organic carbon content in the flotation concentrate. The depressing mechanism of dextrin is described by Liu et al. (2000).

300 g/t of Xanthate was added as sulfide mineral collector. The applied frother is similar to the one used in commercial copper shale ore flotation. A mixture of alcohol and polyethylene glycol ether (150 g/t) acted as the frother. The duration of each flotation test was five minutes. The flotation tests were carried out once with a pre-treatment with 30% ethanol and once without the pre-treatment stage in advance to the flotation conditioning.

The grade-recovery diagram depicted in Fig. 2 shows that the single addition of dextrin leads to a very low Cu recovery, whereas the additional pre-treatment (PT) with ethanol caused an increase of the recovery. The omission of dextrin while retaining the pre-treatment