



Glutamic acid leaching of synthetic covellite – A model system combining experimental data and geochemical modeling

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HIGHLIGHTS

- Covellite is amenable to chemical leaching at neutral to slightly alkaline pH.
- High pH promotes CuS dissolution by glutamic acid and microbial siderophore DFOB.
- Geochemical modelling predicts pH dependent covellite dissolution.

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ABSTRACT

For Kupferschiefer mining established pyrometallurgical and acidic bioleaching methods face numerous problems. This is due to the finely grained and dispersed distribution of the copper minerals, the complex mineralogy, comparably low copper content, and the possibly high carbonate and organic content in this ore. Leaching at neutral pH seemed worth a try: At neutral pH the abundant carbonates do not need to be dissolved and therewith would not consume excessive amounts of provided acids. Certainly, copper solubility at neutral pH is reduced compared to an acidic environment; however, if copper complexing ligands would be supplied abundantly, copper contents in the mobile phase could easily reach the required economic level. We set up a model system to study the effect of parameters such as pH, microorganisms, microbial metabolites, and organic ligands on covellite leaching to get a better understanding of the processes in copper leaching at $\text{pH} \geq 6$. With this model system we could show that glutamic acid and the microbial siderophore desferrioxamine B promote covellite dissolution. Both experimental and modeling data showed that pH is an important parameter in covellite dissolution. An increase of pH from 6 to 9 could elevate copper extraction in the presence of glutamic acid by a factor of five. These results have implications for both development of a biotechnological process regarding metal extraction from Kupferschiefer, and for the interaction of bacterial metabolites with the lithosphere and potential mobilization of heavy metals in alkaline environments.

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1. Introduction

Kupferschiefer of northern central Europe is one of the largest sediment-hosted accumulations of copper ores worldwide, containing more than 60 million tons of copper (Kutschke et al., 2015). Kupferschiefer ore typically consists of the three facies

carbonate rocks, black shale and sandstone in highly variably thicknesses and copper contents (Vaughan et al., 1989; Borg et al., 2012). Copper is always present as finely dispersed sulfidic minerals with grain sizes of 20–200 μm (Vaughan et al., 1989). All three facies tend to have significant though variable carbonate contents (0.07–75%) (Oszczepalski, 1986; Bechtel et al., 2000, 2002; Chmielewski, 2007). Copper concentration by means of flotation is applied to the sandstone and carbonate facies of the ore followed by pyrometallurgical methods with known risks regarding the high arsenic contents (Matlakowska et al., 2012;

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Kutschke et al., 2015). The copper black shale facies is rather problematic for flotation due to high kerogen contents (Kutschke et al., 2015). Additionally, for Kupferschiefer deposits with lower copper contents hydrometallurgical methods such as acid bioleaching might be used. Clearly, high carbonate contents might impede acid bioleaching by acidophilic microorganisms such as *Acidithiobacillus ferrooxidans* (Kiel and Schwartz, 1980; Bosecker, 1997) due to unwanted acid consumption. Considering the general world-wide trend to also mine more complex/lower grade copper ores (Rawlings, 2004; Brierley, 2008), the need for advanced/alternative mining technologies is growing. Microorganisms thriving at circumneutral or slightly alkaline pH (neutrophilic bioleaching) might be a suitable alternative for acid bioleaching of carbonate rich copper ores.

Microorganisms isolated from Kupferschiefer all belong to the group of neutrophilic microorganisms, including the well-known species of the genera *Bacillus*, *Pseudomonas*, *Microbacterium*, *Acinetobacter*, and *Rhodotorula* (Matlakowska et al., 2007; Matlakowska and Sklodowska, 2009). They were shown to adapt to the elevated metal contents of such environments (Matlakowska et al., 2008; Matlakowska and Sklodowska, 2009; Rajpert et al., 2013). Metal mobilization from soils and ores by neutrophilic organisms was shown to proceed by various ways such as production of organic acids, complexing agents, and enzymes (Kiel and Schwartz, 1980; Anjum et al., 2009; Ding et al., 2013). We used a neutrophilic isolate with which our institute has more than a decade of experience and which was isolated from a uranium dump site in Germany (Panak et al., 2000; Selenska-Pobell et al., 2001; Pollmann et al., 2006). For this study we identified it as the neutrophilic bacterial species *Lysinibacillus sphaericus* and show that it fulfils the criteria of being copper tolerant and organic ligand producing. We evaluate the effect of excreted ligands, growth media and that of the model ligand desferrioxamine (DFOB) on copper leaching efficiency. Dissolution and oxidation reactions of copper-containing minerals are quite diverse, show vastly differing kinetics (Watling, 2006) and are influenced by pH, redox potential, presence of ligands, interactions with gangue materials and the specific surface area of the mineral. For achieving a quantitative process understanding of a selected group of key processes, covellite bioleaching by heterotrophic, neutrophilic microorganisms, we aim at establishing a most simple model system for our experimental investigations. This model allows us to study the parameters affecting mineral leaching and to do geochemical modeling of the leaching process. We chose covellite, CuS, as model mineral, since it is one of the main copper sulfide minerals in Kupferschiefer and known to be formed from other copper sulfides during the leaching process (Muszer et al., 2013; Kostudis et al., 2015). This model system bears the additional advantage of later introducing ^{64}Cu as radiotracer into synthetic covellite. To keep this option we used synthetic covellite already here in this study. Synthesized [^{64}Cu]CuS gives the possibility to do positron emission tomography (Kulenkampff et al., 2015, 2016a, 2016b) of column leaching experiments. The usefulness of radiotracer applications in batch and column experiments for gaining enhanced process understanding has been demonstrated in numerous studies (Franke et al., 2008; Hildebrand and Franke, 2012; Mansel and Franke, 2015; Poetsch and Lippold, 2016).

In this work we present the features of our model system including the method of covellite synthesis and characterization, description of the used bacteria, media, and ligand solutions, as well as results of bioleaching and chemical leaching (abiotic leaching) assays. These experimental results are aligned with geochemical modeling data to show that it is possible to simulate the effect of glutamic acid and desferrioxamine B on covellite leaching under neutral to slightly alkaline pH conditions.

2. Materials and methods

2.1. Synthesis of covellite

The covellite used in this study was synthesized, since this gives the opportunity for the introduction of the radionuclide ^{64}Cu ($T_{1/2} = 12.7$ h) in projected tracer experiments. The procedure for microwave-assisted chemical bath deposition of covellite (CuS) was adopted from (Xin et al., 2009). Slow dosage of the reactants, as a prerequisite of regular crystal growth, is achieved by introducing Cu and S in a chemically bound form: As Cu-EDTA complex and as thioacetamide, respectively. For complex formation, 10 mL of 1 M ethylenediaminetetraacetic acid disodium salt solution were slowly added to 10 mL of 1 M copper acetate solution in a beaker glass while stirring. The pH was then adjusted to pH 8 by adding NH_4OH solution in order to facilitate release of S^{2-} from thioacetamide, which was added as a 1 M solution (10 mL). The mixture was made up to a total volume of 50 mL with deionized water, and was contacted with the substrate. Si wafers were vertically fixed at the liquid surface. The reaction was performed in a microwave oven (Severin, Germany), applying a power of 125 W for 45 min. The solution was then discharged, and the substrates were thoroughly rinsed with deionized water to remove non-bound CuS particles.

2.2. Characterization of CuS precipitates on Si wafers

The crystalline structure of the synthetic covellite was investigated using a D8 Advance (Bruker) diffractometer for Bragg-Brentano-geometry and an Empyrean diffractometer for surface sensitive measurements in grazing incidence geometry. Both were equipped with a copper source and a point detector either combined with a secondary graphite monochromator (D8) or a collimator (Empyrean). The expected hexagonal covellite phase was detected. The peak positions in the experiment match those of the literature data whereas the peak intensities differ from the tabulated values indicating a slightly distorted unit cell. In the Bragg-Brentano measurement, a broad peak is clearly visible, which can be attributed to an amorphous fraction of the sample. The grazing incidence measurements show additional peaks between $2\theta = 14^\circ$ and 24° . These peaks of lower intensity could not be assigned to any reasonable phase, checking all Cu–S phases and compounds containing Si or Si oxides. (There was no agreement found within the International Centre for Diffraction Data (ICDD) database.) These peaks appear only on the grazing incidence measurements, i.e., these are phases that appear on the surface of the sample due to a possible contamination/oxidation. The estimated full width half mean (FWHM) of the diffraction peaks gave a value which corresponds to a crystallite size of about 20 nm. According to EDX-measurements, no strong contaminations were found, only additional carbon and oxygen.

2.3. Microorganisms and growth media

The bacterial strain JG-C30 was isolated from the former uranium mine dump Haberland in Johanngeorgenstadt, Germany. Bacteria were grown in iron deficient minimal media containing 25.2 g/L glycerol (Roth, Germany), 10 g/L glutamic acid (Roth, Germany), 5 g/L Na-acetate-trihydrate (Roth, Germany), 0.5 g/L K_2HPO_4 (Merck, Germany), 0.5 g/L KH_2PO_4 (Merck, Germany), 0.2 g/L $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$ (Merck, Germany), 0.008 g/L $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (Merck, Germany), 0.013 g/L $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$ (Merck, Germany), 0.033 g/L $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$ (Merck, Germany), 0.005 g/L thiamine hydrochloride (Merck, Germany) and 0.005 g/L biotin (Sigma-Aldrich, Germany). Sulfates, biotin, and thiamine were prepared separately and sterilized by filtration. Calcium chloride solution and carbon, nitrogen,

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