

## Inhibition of arsenic bioleaching from mining wastes

A. Pawłowska<sup>1</sup>

<sup>1</sup> Department of Process Engineering and Technology of Polymer and Carbon Materials, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland  
agnieszka.pawlowska@pwr.edu.pl

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The extraction and processing of ores generate large amounts of mine waste, most often deposited under atmospheric conditions, where sulfide minerals become thermodynamically unstable and might cause environmental contamination, releasing potentially toxic elements. It is particularly problematic in former mining areas. Oxidative dissolution of sulfides as a result of bioweathering causes acidity, releasing sulfate, iron, and associated metal ions to pore waters, characterised by a low pH (<4), primarily yellow-orange or red colour (Figure 1). The quality of acid mine drainage depends on many factors, including mineralogical and geochemical properties, hydrogeological conditions, and the activity of lithoautotrophic microorganisms (Migaszewski et al., 2016). In Poland, acid waters can be found mainly where coal mining waste or metal ores have been deposited.



Figure 1. Africa reservoir, The Former Coal Mine Babina, Łęknica, Poland (photo by A. Pawłowska)

Mitigating toxic metal release from post-mining wastes under acidic conditions is important. One method is to change the surface characteristics of solids by surfactant adsorption. Similar changes are used in mineral processing, such as flotation or flocculation. The use of surfactants to inhibit ferrous oxidation and simultaneously acid generation by acidophilic bacteria can be found in the literature. The most efficient are sodium dodecyl sulfate (SDS) and sodium lauryl sulfate (SLS) (Kleinmann and Erickson, 1983; Singh and Bhatnagar, 1989). Studies on the role of surfactants in the process of bacterial adhesion to the schwertmannite surface, as a secondary mineral, showed that it is possible to create conditions for bacteria repulsion or attraction to the surface, depending on the surfactant used, which could be applied to control the adhesion and therefore bioleaching process (Pawłowska and Sadowski, 2020). Biosurfactants, such as rhamnolipids, were also studied, but their high cost limits their industrial application. Nevertheless, such compounds have been shown to modify the surface charge of arsenic waste, affecting bioleaching. The presence of lipopolysaccharides on the surface of mineral waste decreased leaching efficiency and favoured secondary product adhesion (Pawłowska et al., 2021).

Currently, there is only an incipient understanding of the interfacial interactions between biosurfactants, mineral surfaces, and microorganisms. Therefore, it is necessary to explain the phenomena that occur in the natural environment to control the side effects of acid mine drainage that are responsible for the release of toxic metals.

The mineral material was taken from a large stockpile of mining waste deposited in the area of the backfilled Jan shaft in Złoty Stok (Poland). A particle size of 1-1.25 mm was used. The presence of löllingite, tremolite, actinolite, phlogopite, albite, and nimite was confirmed by the X-ray diffraction analysis. Elemental analysis was performed by X-ray fluorescence. The waste contained (m/m%): Si 34.3, Fe 20.3, As 8.29, Ca 7.69, Al 5.3, Mg 4.15, K 3.73, and 1.4 S (Pawłowska et al., 2021). As part of the study, a consortium of autochthonic acidophilic bacteria was isolated from waste material. The 16S rRNA gene sequence analysis revealed the dominance of *Acidithiobacillus ferrooxidans* (68.2%) and 31.0% of the *Acidophilum cryptum* group. It confirmed that bacteria responsible for acid mine drainage are present in former mining areas and that toxic ion release can occur under preferable conditions.

Leaching experiments were carried out in shaken flasks for different systems to check the influence of surface-active substances. Each sample assumed 10% solid (w/v). Deionised water and chemical-grade reagents will be used. Microorganisms were grown in medium composed of 3 g (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0.1 g KCl, 0.5 g KH<sub>2</sub>PO<sub>4</sub>, 0.5 g MgSO<sub>4</sub>·7H<sub>2</sub>O, 0.01 g Ca(NO<sub>3</sub>)<sub>2</sub>, 44.8 g FeSO<sub>4</sub>·7H<sub>2</sub>O per litre of deionised water (inoculum 10% v/v, pH 2.0).

During the process, samples were taken to analyse arsenic content, ferrous and ferric iron concentration, redox potential, pH, and specific surface area. Metal concentration was determined using the inductively coupled plasma optical emission spectrometry technique (Agilent 5110 ICP-OES Agilent Technologies, Australia). To understand the interactions between surfactants, solids, and microorganisms, the zeta potential of leaching residues (1-1.25 mm) was determined using a Surpass3 analyzer (Anton Paar, Austria), and solid by-products (fine particles) were measured with the Zetasizer 2000 (Zetasizer, Malvern, United Kingdom) at a constant ionic strength of  $10^{-3}$  M NaCl, pH 2.0.

Initial experiments conducted in columns showed that the presence of anionic surfactant, SDS, inhibited arsenic release from the waste. After three weeks of the process, bioextraction was inhibited by 39.5%. The adsorption of surfactants caused changes in the surface properties of the solids tested. The arsenic-bearing surface charge (-0.45 mV) becomes more negative after contact with SDS (-8.24 mV) due to the presence of negatively charged sulfate polar heads of surfactant. As a result of the bio-oxidation, precipitation of the secondary product occurred (zeta potential 25 mV) leading to positive zeta potential of bioleaching residues (14 mV). This shows that surface modification with surfactants can be a useful tool for controlling heavy metal release from mining waste.

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