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Biologically produced sulphide for purification of process streams, effluent treatment and recovery of metals in the metal and mining industry

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Abstract

One of the best available technologies for the removal of metals from water is in the form of metal sulphides. Metal removal by sulphide precipitation is a well-known process that is characterised by compact residues and very high removal efficiencies. Compared to neutralisation alone the sludge volume is 6 to 10 times lower and the toxic metals are removed to a 0.01–1 ppm level. Furthermore, selective metal precipitation is possible, allowing for separate recovery of valuable metals like copper, nickel, cobalt and zinc from nuisance metals like arsenic and antimony. However, the cost of reagent (NaHS or H_2S gas) and safety aspects are often prohibitive.

This paper describes a novel biological process for safe and cost effective production of sulphide from elemental sulphur, waste sulphuric acid or sulphate present in effluents. With this technology, gaseous or dissolved H_2S is produced on-site and on-demand in an engineered, high rate bioreactor.

Experience with industrial applications at metal processing plants will be presented. The technology can serve to selectively recover metals from e.g. bleed streams, leach liquor, effluent streams and acid mine drainage. Lower overall costs and increased safety (no transport or storage of sulphide, production on-demand and at ambient pressure) are the main advantages of this new process compared to its alternatives.
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1. Introduction

1.1. Origin and problems related to wastes in metal and mining industry

The mining and metallurgical industry generate large volumes of waste- and process water that are polluted with dissolved heavy metals or sulphate, or both. For instance, acid mine and rock drainage is currently one of the most widespread forms of pollution worldwide. In Canada alone, it is estimated that 12,500 ha of tailings and 750 million tonnes of waste rock are present that can release acid and toxic compounds [1]. Acid mine drainage can have a moderate (0.35–0.55 g/l [2]) to high (1.5–7.2 g/l [3]) sulphate concentration. Metals of particular interest in acid mine drainage and industrial wastewaters include copper, zinc, cadmium, arsenic, manganese, aluminium, lead, nickel, silver, mercury, chromium and iron, in a concentration that can range from 10^{-6} to 10^{2} g/l. The composition of such a

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wastewater reflects the particular combination of heavy metals originating from a metallurgical operations. This toxic leachate can cause severe aquatic habitat degradation downstream of the mine when discharged untreated. Slag from metallurgical processes poses a similar problem. Even though it often contains high concentrations of (potentially valuable) heavy metals, it is dumped in landfills or tailings ponds. Depending on the composition of the slag, these metals can be released as a result of weathering of the slag.

Presently, removal by precipitation as metal hydroxide is the most widely used treatment method for water contaminated with heavy metals. This is because of the simplicity and the low costs of this method. For the same reasons, sulphate removal is mostly accomplished by precipitation with Ca^{2+}, added as lime. However, more stringent legislation in future and an increasing scarcity of resources creates a need for heavy metal and sulphate removal technologies with a better performance. Thus, treatment processes should aim to recover valuable metals and other possible resources from waste streams such as sulphur compounds and process water.

1.2. Removal and recovery of metals as metal sulphides

When it comes to sludge volume, reusability of the sludge and effluent quality, precipitation of metals with sulphide is superior to precipitation as hydroxides. It has many advantages over lime precipitation:

- High reactivity of sulphides with heavy metal ions and very low solubility of the resulting metal sulphides over a broad pH range resulting in lower effluent concentrations (see Fig. 1).
- Sulphide precipitation, unlike hydroxide precipitation, is relatively insensitive to the presence of complexes and most chelating agents.
- Sulphide removes chromates and dichromates without preliminary reduction of the chromium to the trivalent state.
- A high degree of selective metal precipitation is possible with sulphide, as opposed to hydroxide precipitation.
- Metal sulphide sludges generally are more dense and stable than metal hydroxide sludges [4], exhibiting better thickening and dewatering characteristics than the corresponding metal hydroxide sludge, which facilitates further processing.

Previous objections against the use of sulphide, i.e. that it is toxic and corrosive, do not hold anymore because of the application of adequate safety measures

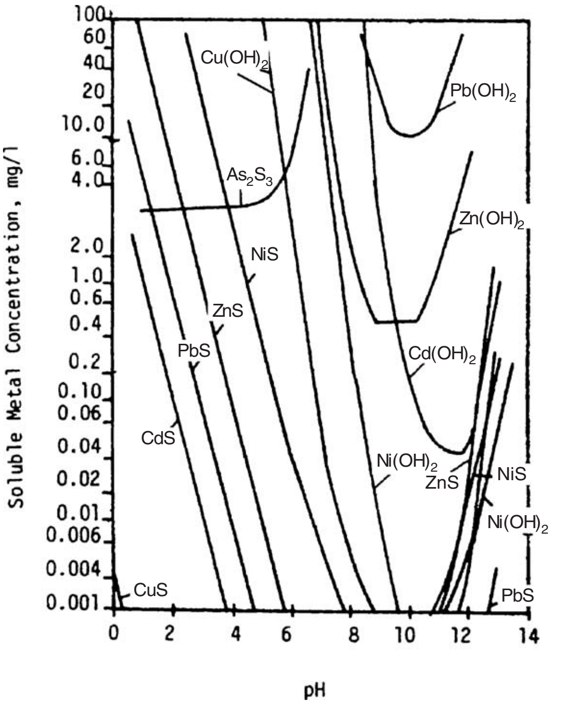

Fig. 1. Comparison between the equilibrium concentrations of metal hydroxides and metal sulphides [5].

and the use of modern corrosion-resistant construction materials (plastics) eliminate these disadvantages. Sulphide precipitation would be the method of choice, if the high cost of transporting, storing or producing sulphide on-site (as NaSH or H_2S) would not have hampered its widespread application in the metal and mining industry. In present applications for heavy metal removal with sulphide, the sulphide needed for precipitation is mostly obtained from chemical sources such as Na_2S, NaHS, CaS, FeS and H_2S.

In the remainder of this paper, technology will be described to produce sulphide on-site and on-demand using biotechnology. This eliminates the hazards and costs that accompany the transport, handling and storage of chemical sulphides.

2. Biotechnological sulphate reduction

The first clue that respiration could be an anaerobic way of life was obtained in 1895 by Beijerinck [6], who showed that sulphate could be reduced to sulphide in sediments. Although many bacteria can produce sulphide, only a few do so at a sufficient rate for application in high-rate processes. These rapid sulphide-generating bacteria are able to conserve energy by the reduction of sulphur oxyanions like sulphate, sulphite and thiosulphate [7], and they are generally termed sulphate-

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