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Hydrometallurgy 83 (2006) 214 – 222

hydrometallurgy

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Product inhibition by sulphide species on biological sulphate reduction for the treatment of acid mine drainage

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Abstract

It is well recognised that the product of sulphate reduction, i.e. the sulphide species formed, may inhibit the biological process. In this paper, we further the kinetic study of biological sulphate reduction using the mixed population of complete oxidisers growing on acetate for which kinetic data has been reported previously as a function of sulphate concentration, temperature, dilution rate and volumetric sulphate loading using chemostat culture by Moosa et al. to provide kinetic insight into this inhibition.

The effect of a feed sulphide concentration in the range 0.50 to 1.25 kg m^{-3} on the biological sulphate reduction process is established using chemostat culture at pH 7.0±0.2. Further, the chemical speciation of sulphide as undissociated H_2S or dissociated HS^- on process inhibition is reported through the variation of operating pH across the range pH 6.0 to pH 7.5 at a sulphate feed concentration of 2.5 kg m^{-3}. It is clearly shown that inhibition is chiefly mediated by the undissociated H_2S sulphide species, rather than the total sulphide concentration. This inhibition was shown to affect the maximum specific growth rate constant and the death rate constant in the Contois rate equation presented previously while having negligible effect on KS describing substrate affinity.

Keywords: Biological sulphate reduction; Sulphide inhibition; Sulphide speciation

1. Introduction

Acid mine drainage (AMD) is a major source of water pollution worldwide with significant cost implications. AMD originates from the bacterially catalysed oxidation of sulphide minerals, most commonly pyrite (FeS_2) [1,2]. This process may occur in operating and abandoned mines, where sulphide minerals are exposed to the atmosphere, as well as in waste rock piles and tailings generated by the processing of mined ore [6]. The oxidation of pyrite is described by:

$$FeS_2 + 3.5\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+.$$

Additional exposure to oxygen, typically at the surface discharge point, results in the oxidation and subsequent hydrolysis of the ferrous iron, generating additional proton acidity. Therefore, the oxidation of one mole of pyrite can ultimately produce four moles of proton acidity, making this one of the most prolific acid generating reactions in nature [7]. The acid generated by these reactions can be responsible for further leaching of acid labile minerals resulting in a "classical" AMD discharge, having a low pH, high

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doi:10.1016/j.hydromet.2006.03.026

sulphate and iron loading and potentially dangerous levels of other metals.

While a number of treatment options have been proposed for the remediation of AMD, the use of biological sulphate reduction (BSR) is increasingly of interest. In this process, sulphate is reduced biologically to sulphide species, which may either precipitate accompanying metal species or be partially re-oxidised to elemental sulphur. In order to provide necessary design data for BSR processes, adequate kinetic data and its modelling are required. Modelling of the kinetics of BSR as a function of sulphate concentration, temperature, dilution rate and volumetric sulphate loading has been published for both mixed and monocultures of SRB, including our previous studies [3–5]. While it is recognised that the reduction product, sulphide, may inhibit this process [1,2], a review of the literature shows that the effect of sulphide speciation and sulphide concentration on sulphate reduction kinetics have not been elucidated rigorously and limited kinetic data are available with respect to this product inhibition.

The hydrogen sulphide product resulting, in the absence (or limiting presence) of metal species, may dissociate according to the equilibrium reactions given in Eqs. (1) and (2). In the pH range 6 to 8, hydrogen sulphide exists as a mixture of H_2S and HS^- (Fig. 1). Below pH 6, the undissociated form (H_2S) dominates. Dissociated hydrogen sulphide dissociates further to S^{2-} near pH 12.

$$H_2S \Leftrightarrow HS^- + H^+ \qquad (1)$$

$$HS^- \Leftrightarrow S^{2-} + H^+ \qquad (2)$$

Total hydrogen sulphide concentration can be determined by the relationship:

$$H_2S_{\text{total}} = H_2S_{(\text{aq})} + HS^- \qquad (3)$$

or where all reduction of sulphate to sulphide accumulates as hydrogen sulphide:

$$H_2S = (SO_4^{2-})_{\text{influent}} - (SO_4^{2-})_{\text{effluent}}. \qquad (4)$$

While the SRB have the highest tolerance to sulphide of anaerobic microorganisms, their activity is inhibited by its presence [2,8–12]. Two hypotheses are proposed for the mechanism of sulphide inhibition. In the first, metal sulphides precipitate such that the SRB are deprived of essential trace metals required as cofactors for their enzyme systems [13]. In the second, the sulphide is absorbed into the cells and denatures proteins by acting as a cross-linking agent between the polypeptide chains [14] and interfering with the metabolic coenzymes through sulphide bond formation. This theory was challenged by Parkin and Owen [15]. Sulphide inhibition has been shown to be reversible [16,17]. In contrast to other microorganisms where only the undissociated form of hydrogen sulphide (H_2S) is inhibitory, it is debated whether total sulphide or only dissociated hydrogen sulphide (H_2S) is inhibitory to SRBs [1,18].

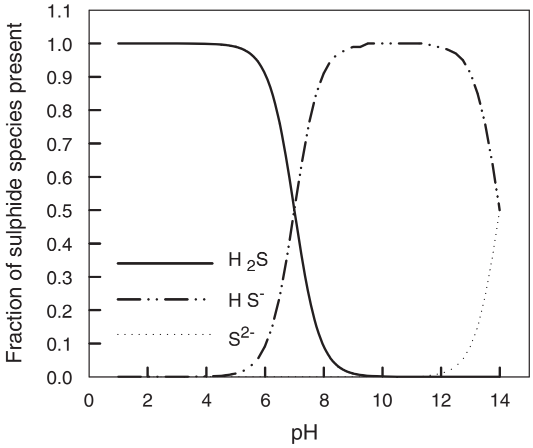

Fig. 1. Relationship between the species of hydrogen sulphide and pH.

Owing to the successful implementation of anaerobic sulphate reduction on a large scale being dependent on the understanding of the reaction kinetics and the effect of inhibitory compounds on the process kinetics, a rigorous study of the effects of sulphide speciation and concentration on the rate and extent of anaerobic sulphate reduction is presented here. The objectives of this study were two-fold, centred on providing a rigorous understanding of the sulphide species mediating sulphide inhibition of bacterial sulphate reduction and on determining the critical total soluble sulphide concentration and concentration of pertinent sulphide species at which this inhibition was mediated. These were achieved by investigating the kinetics of anaerobic sulphate reduction in continuous stirred tank reactors. To achieve a good spread of the ratio of soluble sulphide species present, four pH values were chosen to allow the interconnectedness between pH and sulphide speciation to be realised. These pH values of 6.0, 6.5, 7.0 and 7.5 were selected over the range in which the most significant transition from the undissociated form of H_2S to the dissociated form HS^- is observed (Fig. 1) and studied at a fixed sulphate feed concentration in the absence of added sulphide. Under