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Equation for thiosulphate yield during pyrite oxidation

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ABSTRACT

A pyrite concentrate with a grind size P_{80} of 14 μm was oxidized in an alkaline medium at an oxygen overpressure between 10 and 40 psig, at a temperature of 80 °C. Sodium hydroxide was used to neutralize the acid produced as a result of pyrite oxidation. When the pH was maintained above 12.5, there were three dominant sulphur oxyanions detected in the solution, thiosulphate, sulphite and sulphate.

The focus of this study was the calculation of thiosulphate yield as a function of sulphide sulphur concentration of the pyrite in the feed. This calculation included the effect of other sulphur oxyanions on the thiosulphate yield since it is well known that thiosulphate oxidizes fairly rapidly to tetrathionate and trithionate and higher sulphur oxyanions under high alkalinity conditions. The transient formation of tetrathionate and trithionate can only be estimated when the mechanism of formation of these oxyanions is known. Various schemes involving branching of the reaction pathways can be found in the literature but unfortunately, no widely accepted mechanism has emerged from these studies.

In the present study, the transformation mechanism is based on the least electron transfer principle and assumes that the transformation reactions occur in series. Based on this approach, linear equations were derived and used to set up a kinetic model of the system with respect to thiosulphate yield. In determining the kinetic constants, the presence of unseen and unmeasured intermediates was assumed and calculated based on the corresponding reaction stoichiometry. A single rate expression combining kinetic constants of all the metastable oxyanions was derived to predict the thiosulphate yield as a function of the known pyrite sulphide sulphur concentration under the experimental conditions that were adopted.

$$\frac{dC_{S2O3}}{dt} = 2^{-1}k_1k_2[C_os^{-2}][P_{O_2}]^{\propto 1}[OH]^{\beta 2}\{1 - k_4[P_{O_2}]^{\propto 4} + 2^{-3}k_4k_5[P_{O_2}]^{\propto 4}[OH]^{\beta 5}(5 + k_6[OH]^{\beta 6})\}$$

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1. Introduction

Pyrite is an abundant sulphide mineral that often contains gold as extremely fine (<1 μm) particles trapped in the host mineral. In most instances, it is necessary to decompose the pyrite to liberate and recover the contained gold, carrier (gangue) mineral. The popular route for decomposition of sulphide minerals is through oxidation by molecular oxygen. Depending on the conditions applied, the nature of the oxidation products might differ substantially. When there is no additional reagent included, the oxidation leads to aqueous ferrous/ferric ions and sulphate. But in the presence of sodium hydroxide, the oxidation of pyrite forms goethite or amorphous iron oxide as a solid product and various aqueous sulphur oxyanions. The consumption of NaOH in these reactions can be very high and render the process uneconomical. However, this cost would be reduced if conditions could be found in which the lixiviant for gold is formed at the same time as the sulphide oxidation reactions. The potential for thiosulphate formation in parallel to sulphide oxidative decomposition was the main focus of this study.

Extensive studies of the solid products formed during atmospheric alkaline oxidation of pyrite at temperatures from 50 to 85 °C were conducted by Ciminelli (1987) and Caldeira et al. (2003), who concluded that the precipitation occurs mainly in bulk solution, resulting in the formation of a stable colloidal suspension of the oxidation products. These workers claimed that the pyrite particles are initially covered by a thin oxide layer which then breaks down quite rapidly, so does not inhibit the further oxidation

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reaction. Ciminelli (1987) described the kinetics of pyrite oxidation in NaOH solution as being under a core model under chemical reaction rate control at the mineral surface. A similar observation was made by Burkin (1969), who observed a linear rate (often associated with chemically controlled mechanism) of pyrite oxidation in strong alkaline solution at temperatures of 60–120 °C. He suggested that the oxide layer separates during the oxidation reaction, exposing fresh surface to the reactants. Based on this knowledge, it is not anticipated that the kinetics of pyrite oxidation in NaOH solution will be inhibited by a product layer.

The oxidative conversion of the sulphide sulphur in pyrite is complex in NaOH solution, and the reaction is generally far from being in equilibrium. The occurrence of several metastable aqueous sulphur species has been reported by various researchers (Goldhaber, 1983; Mishra and Osseso-Asare, 1988; Druschel, 2003; Chen and Morris, 1972; Zhang, 2004) but there is no consistent (or common) mechanism for the sulphur oxygen reaction during pyrite oxidation known.

The oxidation of sulphide to sulphate is an 8-electron process, but it is unlikely that more than two electrons are transferred in any one reaction step (Basolo and Pearson, 1967 after Williamson and Rimstidt, 1992; Fleming, 2003, 2014). Therefore, oxidation of sulphide might be viewed as a chain reaction with the stepwise increase of oxidation state of sulphur: $S^{-2} \rightarrow S^{o} \rightarrow S^{+2}_{(S2O3)} \rightarrow S^{+2.5}_{(S4O6)} \rightarrow S^{+3.3}_{(S3O6)} \rightarrow S^{+4}_{(SO3)} \rightarrow S^{+6}_{(SO4)}$. The intermediate species in this chain of transformation have all been identified (Chen and Morris, 1972; Goldhaber, 1983; Rimstidt and Vaughan, 2003; Lyons and Nickless, 1968; Rolla and Chakrabarti, 1982) in solution during pyrite oxidation, and certain species have shown metastable persistence under specific conditions.

An important factor for achieving a favourable species distribution in a non-equilibrium system is the rate of conversion of one species to another. In pursuing a maximum thiosulphate yield for effective gold leaching, the most important reactions to consider are the oxidation of thiosulphate and the hydrolysis of tetrathionate and trithionate. The oxidation of thiosulphate reduces the available thiosulphate for gold leaching while the hydrolysis of tetrathionate and trithionate regenerates thiosulphate.

The oxidation of thiosulphate at elevated temperature and pressure produces sulphate as a final product. However, the course of the reactions leading to sulphate is largely dependent on kinetic factors rather than thermodynamic consideration, as reported by Gluud (1921), Forward et al. (1964) and Rolla and Chakrabarti (1982). The rate of thiosulphate oxidation increases with increasing temperature, and also shows pseudo-first-order kinetics with respect to thiosulphate concentration (Rolla and Chakrabarti, 1982).

The hydrolysis of tetrathionate generates thiosulphate and trithionate under alkaline pH conditions (Nicol and Melley, 2002; Byerley et al., 1973; Fave and Bresadola, 1955; after Ahern et al., 2005, 2006), the latter being further decomposed to produce thiosulphate and sulphite (Kurtenacker et al., 1936; Goehring et al., 1949; Fave and Divo, 1953, 1954 after Zhang and Dreisinger, 2002). The kinetics of tetrathionate decomposition shows first order dependency with respect to both tetrathionate and hydroxide in the pH range of 10–11.5, as reported by Zhang and Dreisinger (2002). A similar observation was made by Ahern at el (2005, 2006), while studying the kinetics of trithionate degradation in alkaline solution. A linear decrease in trithionate concentration corresponded to a linear increase in thiosulphate concentration. The reaction was found to be first order with respect to trithionate concentration.

Studies investigating the hydrolysis reactions of tetrathionate and trithionate as a single reaction, observed a significant increase in the rate with an increase in pH. It was even reported that the rate was so fast as to be impossible to measure (by initial rate method) when running experiments at pH 12 and higher (Ahern et al., 2005). Hence, there is evidence to suggest the transition of tetrathionate through trithionate to sulphite (while forming thiosulphate as a secondary product) is very rapid at pH > 12. Consequently, when high alkalinity persists, the sequence of reactions from tetrathionate to sulphite is one directional and irreversible to a certain extent, and it is reasonable to suggest a linear one directional conversion concept (stepwise increase of oxidation state of sulphur) as shown above.

In this paper, a simple network of reactions that are all of first order with respect to sulphur oxyanions is proposed as the oxidation pathway of pyrite sulphide sulphur to the final product of sulphate. To explain the kinetics of each reaction, it is assumed that a sequence of elementary reactions occurs, but the intermediates formed cannot be measured because they have short lifetime and are only present in very minute quantities due to rapid transformation. Development of rate equations was based on theoretical consideration (linear change of oxidation state through least electrons transfer and published stoichiometry of reactants) as well as an empirical curve-fitting procedure. The value of the rate constants of the kinetic equations was estimated by calculating the unobserved intermediates by following the concentration (yield) of each species during the pyrite oxidation reaction.

2. Materials and methods

Pyrite concentrate with a grind size P_{80} of 14 μm was used in the current study. The concentrate contained 45.7% sulphide, representing the total sulphur in the sample. The experiments were performed in a sealed 3L glass reactor suitable for a low pressure testing. The reactor was equipped with a pressure gauge, agitation and sampling ports. The oxygen pressure was introduced through the inlet port and flashed by an off-gas line. The reactor was placed in a heating mantle connected to the temperature controller. The temperature, pressure, and agitation were controlled throughout the test. The agitation was fixed at 255 rpm, the temperature maintained at 80 °C, and the oxygen over pressure was varied between 10 and 40 psi. The schematic representation of the reactor is given in Fig. 1. At the start, 100 g of pyrite concentrate was added to one litre of 29 g/L NaOH solution. Thereafter, drops of sodium

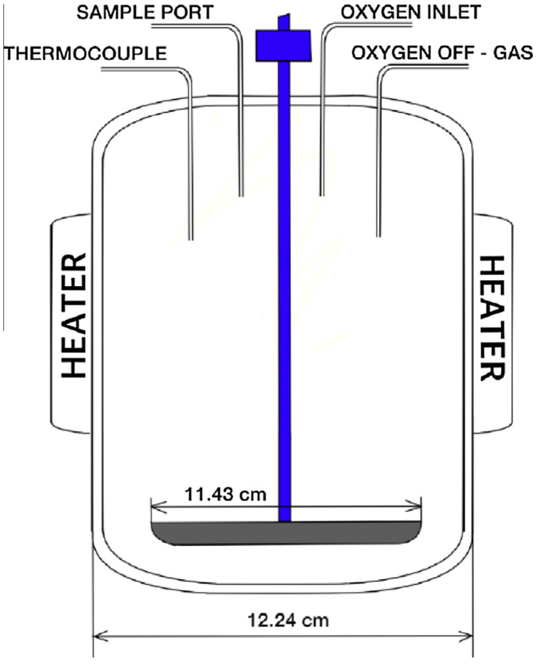

Fig. 1. Schematic of reactor used in the present study.

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